Refinery Integration of By-Products from Coal-Derived Jet Fuels

SEMI-ANNUAL PROGRESS REPORT

April 18, 2005 – October 17, 2005

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Date Issued: November 17, 2005

Grant DE-FC26-03NT41828

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Abstract

This report summarizes the accomplishments toward project goals during the first six months of the second year of the project to assess the properties and performance of coal based products. These products are in the gasoline, diesel and fuel oil range and result from coal based jet fuel production from an Air Force funded program. Specific areas of progress include generation of coal based material that has been fractionated into the desired refinery cuts, acquisition and installation of a research gasoline engine, and modification of diesel engines for use in evaluating diesel produced in the project. The desulfurization of sulfur containing components of coal and petroleum is being studied so that effective conversion of blended coal and petroleum streams can be efficiently converted to useful refinery products. Evaluations to assess the quality of coal based fuel oil are reported. Coal samples have procured and are being assessed for cleaning prior to use in coking studies.

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Refinery Integration of By-Products from Coal-Derived Jet Fuels

Introduction

This program is investigating the fate of each major product from a refinery complex, except jet fuel, resulting from the refinery integration of coal-derived jet fuel production via a combined RCO/LCO strategy by studying the physical and chemical nature of all products that are perturbed by introduction of coal components into the refinery.

The impact of the proposed research is to provide the scientific and fundamental engineering basis to integrate the production of coal-based jet fuel into existing refinery operations in a time frame consistent with availability and economic forecasts related to petroleum-derived as opposed to coal-based feedstocks. The results of these studies lead to the integration of all non-jet-fuel streams into current refinery operations in concert with desired production of coal-based jet fuel engine testing toward the end of the first decade of the new century. For successful utilization of coal-based jet fuels all non-jet-fuel components must fit existing and future product stream specifications.

Executive Summary

Penn State has been working for more than a decade on the development of an advanced, thermally stable, coal-based jet fuel, JP-900. Two process routes to JP-900 have been identified, one involving the hydrotreating of blends of refined chemical oil (a by-product of the coal tar industry) with light cycle oil, and the other involving the addition of coal to delayed cokers. However, no refinery is operated for the primary purpose of making jet fuel. The conversion of the jet fuel section of a refinery to production of coal-based JP-900 would necessarily impact the quantity and quality of the other refinery products, such as gasoline, diesel fuel, fuel oil, and coke. The overall objective of this project is to examine the characteristics and quality of the streams *other than the jet fuel*, and to determine the effect those materials would have on other unit operations in the refinery.

The present report documents the activities of the first six months of year two of what is envisioned to be a four-year program. Our collateral work on jet fuel, funded by the Air Force Office of Scientific Research, is focused exclusively on that product. Thus as we branch out into the study of the other refinery streams, under this present contract, much of the initial effort has necessarily been devoted to equipment acquisition and installation, and to the first experiments.

The overall project involves pilot-scale production of materials at PARC Technical Services (Harmarville, PA). The coal-based gasoline and diesel fuel will be evaluated in appropriate internal combustion engines. Desulfurization, denitrogenation, and saturation of aromatics will be tested. The coal-based fuel oil will be tested in a research boiler. The pitch and coke produced will also be characterized. These interrelated activities are designed to evaluate the full range of products from coal-based thermally stable jet fuel production and to lead toward process integration in existing refineries.

The hydrotreatment of blends of refined chemical oil and light cycle oil, followed by fractionation of the total product, has been performed at PARC. The various distillation cuts have been provided to the researchers at Penn State for analytical characterization and for use in the appropriate evaluation tests. In addition, decant oil was hydrotreated at several levels of severity for use in the co-coking work.

For evaluation of gasoline quality and performance, we have acquired and installed a Ricardo Hydra single-cylinder research engine. The engine can now operate under load and on fuels of interest. Work is continuing on instrumentation and facilities hook-up to the engine test stand.

To assess the impact on diesel fuel quality and performance, two existing engine test stands, using Navistar and DCC turbodiesel engines were enhanced. In addition, new instrumentation for testing ignition quality was purchased and is being installed. The ignition quality test has recently become an ASTM method; we will participate in a

round-robin evaluation of this test, which will provide a useful external comparison of data on the coal-based fuels at no additional cost to the project.

The desulfurization of 4,6-dimethyldibenzothiophene and of dibenzothiophene in decalin was studied over commercial cobalt-molybdenum and nickel-molybdenum catalysts. Quinoline was used as a model compound to investigate the effect of the presence of nitrogen compounds of the desulfurization process. The desulfurization can be explained by pseudo-first-order kinetics, and is strongly inhibited by the presence of quinoline. A flow reactor was designed and constructed for saturation of aromatics. The first series of experiments involved palladium on various supports as the catalysts for saturation. Selective methylation of 2-methylnaphthalene with methanol has been studied for the production of 2,6-dimethylnaphthalene, which would be a value-added coal-based by-product for the petrochemical industry.

For fuel-oil evaluation, a high-temperature in-furnace camera was procured and installed in a water-tube research boiler. Shakedown tests of the camera were completed and preliminary evaluations of fuel oil are reported.

Samples of as-mined coal and of froth flotation products from a Consol mine in Washington County, Pennsylvania were obtained. These materials were used in co-coking experiments. Some of the froth flotation products still have significant ash yield, suggesting that secondary cleaning processes may be necessary to have a low-ash feed to the coker. A pitch product has been isolated by distillation of the heavy distillate from a co-coking experiment. Characterization of these materials is in progress.

Experimental

The respective experimental details for each of the tasks of this project are described within the individual Tasks I – V detailed later in this report.

Results and Discussion

The results of each task of this project are documented and discussed within the appropriate Task I – V detailed later in this report.

Conclusions

Each of the individual tasks of this project has progressed as proposed or to a greater extent than originally proposed. Each task individually contributes to the ultimate goal of refinery integration. This report describes the procurement of equipment into the appropriate laboratories, the establishment of experimental procedures and the generation of early results that indicate the relevance and feasibility of the proposed work. Progress has been made to produce hydrotreated products, differing from conventional refinery products but also compatible with conventional materials. A new approach has generated similar materials not having the added cost of hydrotreating. These materials will be evaluated in the next reporting period and be compared with extensively hydrotreated gasoline, diesel and fuel oil fractions. Engines have been installed which will provide detailed performance measurements on both the gasoline and diesel components in this process. Equipment to provide detailed understanding of the quality of fuel oil has been procured as has equipment needed to study the heavy components available through the process of generating the desired fuels within a conventional petroleum refinery complex.

Technical Discussion

Background

Penn State has been involved in a multi-phase fifteen-year program to develop an advanced thermally stable jet fuel for the Air Force [1-1 -1-4]. This fuel would resist breaking down at high temperatures (900°F), so it could be used for cooling sensitive parts on high-performance aircraft, as well as providing the propulsion. It is provisionally called JP-900.

At its inception, the JP-900 program presumed that this new fuel would be made entirely or substantially from coal. There are three reasons for this.

Scientific validity. Penn State's researchers have shown clearly that the kinds of chemicals in the fuel that make it stable at 900°F (hydroaromatics and naphthenes) can be derived in abundant amounts from coal. This has been demonstrated in numerous peer-reviewed publications [1-5 – 1-10].

Long-term security. Unlike petroleum, coal is a secure, domestic energy resource, for which centuries' worth of reserves remain in the U.S.

Stable procurement. Both petroleum and natural gas are vulnerable to significant price spikes. In contrast, coal companies are willing to write twenty-year delivery contracts at a guaranteed stable price. In turn, this would help stabilize the price of military fuel for decades to come.

To ultimately produce an advanced thermally stable coal-based jet fuel a practical and economically viable process, compatible with current refinery practice, is necessary. The evaluation of this scenario is the subject of this proposal. No refinery is operated for the specific purpose of making jet fuel. Furthermore, refineries are highly integrated, in that many of the individual operations are dependent on, or use streams from, other operations. Therefore, in order to insure that the production of coal-based JP-900 in the jet fuel section of a refinery is acceptable to refinery operators, it is crucial to have data showing the effect of the by-products from coal-based JP-900 production (i.e., the <180°C and the >270°C fractions) on the quantity and quality of the other refinery products: gasoline, diesel, fuel oil, pitch, and coke.

Options for integrating coal, or a coal liquid product that is currently available commercially (a by-product coal tar distillate from the metallurgical coke industry) into existing refineries are illustrated in **Figure 1-1**. With respect to the first two options, coal can either be added to the coker directly or be co-processed with the resid. Of these, addition of the coal to coker has been selected – in consultation with our refinery partner – as the better option to produce sufficient quantities of coal-based fuel for thermal stability and combustion testing. Each of these approaches has a unique set of technical challenges in terms of specifying the proper feedstocks (for both petroleum- and coal-based components), process conditions (temperature and pressure) and processing approaches.

Previous work at Penn State has resulted in significant progress in identifying the remaining critical barriers to realization of coal-based fuels [1-11 – 1-20].

Figure 1-1. Possible Integration of Coal into Existing Refineries.

Objectives

A number of potential JP-900-type jet fuels have been produced by Pennsylvania Applied Research Corporation (PARC) from the hydrotreatment of a coal-derived refined chemical oil (RCO) and its mixture with a petroleum-derived light cycle oil (LCO).

The overall objective of this project is to examine the characteristics and quality of the streams other than the jet fuel, and what effect those materials would have on the

other unit operations in the refinery, the quality and value of the other products. Broadly, these additional by-products are the liquids lighter and heavier than jet fuel itself, i.e., the $<180^{\circ}\text{C}$ and the $>270^{\circ}\text{C}$ fractions produced after hydrotreating the RCO/LCO blend and fractionating to recover the jet fuel and other refinery streams.

Prior to the beginning of this project, virtually all work was focused on the jet fuel. However, as we have noted above, no refinery is run for the specific purpose of making jet fuel. Therefore, to make these processes acceptable for adoption in refineries, it is vital to assess their impact on the other major operations and products in a refinery. The acquisition of that knowledge is the basis of this project.

These studies will impact all of the major product streams in a conventional petroleum-based refinery. Therefore, replacing petroleum feedstock with domestic coal, gasoline, diesel, fuel oil and pitch components will favorably impact reducing dependence on, and security of supply of, foreign petroleum resources.

The objectives of the project are to:

- Investigate and develop an understanding of the most promising refinery integration of all process streams resulting from the production of coal-based jet fuel.
- Demonstrate the quality of each of the process streams in terms of refinery requirements to maintain a stable, profitable refinery operation.

- Demonstrate the performance of key process streams in practical testing used for application of these streams.

This fundamental research was proposed as a four-year program. In this document we report activities and accomplishments for the first half of the second contract year. The approach chosen draws on previous work that has now successfully produced a coal-based JP-900 fuel at pilot-plant scale for initial investigations in the fuel stabilization and combustion studies [1-21 – 1-23]. In that work, it has been shown that hydrotreated blends of light cycle oil and refined chemical oil (a coal-derived liquid) resulted in the most thermally stable product to date.

This program is investigating the fate of each major product from a refinery complex, except jet fuel, resulting from the refinery integration of coal-derived jet fuel production via a combined RCO/LCO strategy by studying the physical and chemical nature of all products that are perturbed by introduction of coal components into the refinery.

The impact of the proposed research is to provide the scientific and fundamental engineering basis to integrate the production of coal-based jet fuel into existing refinery operations in a time frame consistent with availability and economic forecasts related to petroleum-derived as opposed to coal-based feedstocks. The results of these studies lead to the integration of all non-jet-fuel streams into current refinery operations in concert

with desired production of coal-based jet fuel engine testing toward the end of the first decade of the new century. For successful utilization of coal-based jet fuels all non-jet-fuel components must fit existing and future product stream specifications.

Coal tar fractions have been successfully demonstrated to be suitable feedstocks for the production of jet fuels for high-speed aircraft [1-22, 1-23]. The jet fuel, as prepared and evaluated in our Air Force project, is a 180-270°C product, cut from a mixture of RCO/LCO total liquid product. Of this product the <180°C cut represents ~4% of the total product and the >270°C fraction represents just over 40% of the total liquid product [24]. These streams must either be blended as is, chemically converted and then blended, converted to chemicals, or used as feed to the coker.

Scope of Work for Year 3

The technical approach consists of five carefully planned goals whose successful completion will lead to the achievement of the project objectives. These goals include:

- pilot-scale fuel production at PARC,
- evaluation of coal-based gasoline and diesel products in internal combustion engines,
- desulfurization, and denitrogenation of coal-based fuels, the saturation of aromatics to improve stability and the development of chemicals from coal,

- evaluation of coal-based fuel oil, and
- evaluation of pitch and coke materials from coal-based fuel production.

These interrelated goals are designed to evaluate the full utilization of products from coal-based thermally stable jet fuel production and lead toward process integration into existing refineries.

Tasks to be Performed

We are critically analyzing the performance and value of the streams produced from combination of coal-derived components and normal refinery process streams.

The critical analyses include:

- evaluation of gasoline range material in spark-ignited gasoline engines
- evaluation of diesel-range product for use in compression-ignited diesel engines
- evaluation of heavier range materials as heating oils and boiler fuels
- evaluation of products from co-coking strategies as precursors to higher value cokes and carbons.

The following summarizes the technical achievements for the first six months of the second project year.

Task 1. Pilot-Scale Fuel Production at PARC

(G. Wilson (PARC), L. Rudnick (PSU))

Subtask 1.1 LCO and RCO Procurement

Light cycle oil (LCO) was procured from United Refining Company in Warren, PA. Refined chemical oil (RCO) was procured from Koppers, Inc., Harmarville, PA. These materials were blended to provide a feedstock RCO/LCO blend that was upgraded by deep hydrotreatment and fractionated in subsequent tasks. Simulated distillation (D2887) of LCO and RCO samples is shown in **Table 1-1**.

**Table 1-1 United LCO and Koppers RCO
Simulated Distillations**

SAMPLE	LCO PR 1244	RCO PR 1238	1:1 RCO:LCO PR 1251
Instrument	5880	5880	5880
IBP	350	335	341
5%	451	390	396
10%	485	429	431
20%	516	433	436
30%	533	435	440
40%	553	437	486
50%	570	438	534
60%	593	451	551
70%	618	500	577
80%	651	545	625
90%	684	598	667
95%	705	650	704
FBP	771	894	813
% at 356F (180C)	0.15	1.91	1.36
% at 518F (270C)	31.2	74.0	45.5
% at 572F (300C)	50.9	85.1	68.1

Subtask 1.2 Catalyst Preparation

Catalyst, necessary for the deep hydrotreating of total liquid product (TLP), was obtained in this task. In previous work [1-1, 1-24], PARC has identified a Criterion Syncat-3 cobalt-molybdenum or Syncat 37, nickel-molybdenum catalysts as effective in converting the coal-based blend to a deeply hydrotreated total liquid product. This product has been found to be rich in hydroaromatic components and as a result the jet fuel is thermally very stable. These catalysts must be activated by presulfiding after drying in a flow of hydrogen. The SYNCAT catalyst is received by PARC pre-

impregnated with a sulfur compound, however, PARC employs a treatment with kerosene containing 0.25 wt% dimethyldisulfide to ensure proper sulfiding prior to use.

Subtask 1.3 Hydrotreatment of Blended Product

Production of deeply hydrotreated total liquid product (TLP) to provide material for other tasks in this project by large-scale production of TLP is necessary. The production of drum quantities of liquid products is described below including details for the hydrotreatment, hydrogenation and fractionation of total liquid product into fractions to be evaluated in this program. The non-jet-fuel components co-produced with the jet fuel were isolated by fractional distillation for further characterization and testing at Penn State University.

The scope of this project was to produce hydrogenated total liquid products (TLP) to generate 180°C- naphtha, 180-270°C high stability jet fuel that meet the tentative specifications set for JP-900, 270-343°C diesel and 343°C + fuel. The jet fuel target production of this project was 500 gallons.

The hydrogenation catalyst used in this project was Engelhard's REDAR catalyst. The charge for the unit was as follows:

Hydrogenation	Reactor 1	2251 cc, 1657 gm, Engelhard REDAR (PC-765)
	Reactor 2	2832 cc, 2084 gm, Engelhard REDAR (PC-765)

Two different feeds were used in this project. The first feed consisted of three individual drum blends of double passed hydrogenated full boiling range P63-127 product from the previous 2004 program No 10. These blends, X-1099, X-1100 and X-1101 were distilled to remove the 550°F+ material before being further hydrogenated in this program. The corresponding 550°F- fractions contained respectively 4.2, 11.1 and 21.3 wt% tetralin and no naphthalene. They were further hydrogenated yielding almost completely hydrogenated components with a decalin content of 35.3 wt% and a residual tetralin content of < 1 wt%. This material was subsequently distilled to remove the gasoline fraction. The jet fuel product from this run was identified as SR-0225.

The second feed (PARC SR 0224) was a blend of 180-270°C (356-518°F) jet fuels produced in earlier programs by hydrotreated at different severities. The individual hydrotreated jet fuels making up this blend had not been previously hydrogenated. SR-0224 contained 32.2 wt% tetralin and 198 ppm nitrogen. The high nitrogen content required two passes over the hydrogenation catalyst to obtain < 1 wt% tetralin in the product. The decalin content in the hydrogenated product, SR-0226, was 44.4 wt%.

In the course of this study jet fuel samples with varying smoke points and related aromatics contents were sampled to Penn State for determination of their thermal stability. It was determined that for the jet fuel to meet the smoke point specification of JP5, JP-8 and therefore JP-900 the residual aromatics content must be reduced to a very low level, probably < 2 wt%.

Work at Penn State had also determined that a final treatment of the jet fuel over a bed of either activated alumina or activated clay improved the thermal stability even further than hydrogenation alone. Consequently it was decided to blend all of the hydrogenated jet fuel and subject it to clay treatment using Engelhard F-24 clay. This treatment changed the visual color from amber to water white and decreased the amount of carbon produced in the thermal stability test. The final clay treated product was identified as SR-0227CT.

Pilot unit description

PARC's adiabatic unit, P67 was used in this project. This unit uses an adiabatic system to control heat loss in the first reactor while the second reactor is used as a pseudo adiabatic system via isothermal controls keeping a temperature gradient across the reactor. A simplified flow diagram is shown in **Figure 1-2**. The catalyst loading diagrams are shown in **Figures 1-3 and 1-4**.

P63/67 SIMPLIFIED PROCESS FLOW DIAGRAM

Figure 1-2

P63-67 #1 Reactor Layout

Figure 1-3

P63-67 Reactor 1 Charge Sheet

Catalyst Bed Measurements and Thermocouple Locations

Run No.: P67-76

Date: 10/12/04

Catalyst ID.: PC - 765

CC's Loaded: 2251

Grams Loaded: 1657

Tap Density: 0.736

Loaded By: MDM

Catalyst Bed

Quartz

Figure 1-4

The reactor outlet product was separated in the hot, high-pressure gas-liquid separator in to gas and liquid products. The liquid product was then sent to the fractionation tower where it was stripped of H_2S and ammonia, exiting the unit as total liquid product (TLP). The tower system was run at atmospheric pressure.

The separator off-gas was passed through an amine scrubber to remove H_2S . The scrubber outlet gas is combined with make-up hydrogen to constitute the inlet gas stream. This mixed gas stream is sampled by the on-line gas chromatograph. The inlet gas was premixed with the feed before entering the preheater of the first reactor. The unit was operated in recycle gas mode, typically with a minimum of 98% H_2 in the inlet gas stream.

(A) Preparation of hydrogenation feeds

Distillations (150-gallon still)

It was decided that the $550^\circ\text{F}+$ material in the product from Program 10 was reducing the efficiency of the catalyst. This material needed to be distilled in order to remove the $550^\circ\text{F}+$ fraction. The still used to distill the product was a batch still that holds a 150-gallon charge of material. Three runs on this still were needed to process the entire product.

The first distillation (X-1099) was going to remove both the $356^\circ\text{F}-$ and the $550^\circ\text{F}+$ fractions. This would leave only the jet fuel cut to be hydrogenated. However,

each of the cuts taken to create the 356°F cut point were essentially the same. Because of the inability to differentiate between the 356°F- and 356°F+ fractions, both fractions were blended and sent to P67. The other two distillations (X-1100 and X-1101) went as planned and only the 550°F+ material was removed before being sent for hydrogenation in P67. The total amounts of each cut are shown below.

	X-1099	X-1100	X-1101
550°F-	124.8	134.6	119.2
550°F+	22.5	34.2	29.8

All values are in gallons

(B) Hydrogenation operations and results

Catalyst reduction

PARC's adiabatic unit P67 was charged with Engelhard REDAR precious metals hydrogenation catalyst, PC-765, in amounts shown below. The No 1 reactor was loaded with inert material in the quench zones as indicated in **Figure 1-5**.

P67 Second Reactor Charge Sheet

Catalyst Bed Measurements and Thermocouple Locations

Run No.: P67-76

Date: 10/12/04

Catalyst ID.: PC - 765

CC's Loaded: 2832

Grams Loaded: 2085

Tap Density: 0.736

Loaded By: MDM

Figure 1-5

This figure also shows the arrangement of heater blocks relative to the first reactor.

Reactor 1	2251 cc	1657 gm
Reactor 2	2832 cc	2084 gm
Total	5083 cc	3741 gm

The catalyst was reduced prior to introducing run feed. Hydrogen was introduced at a flow rate of about 66 scf/hr at the minimum pressure possible for unit pressure control (about 115 psig). Low pressure and once through hydrogen was used to avoid the potential for agglomeration of catalytic metal atoms in a steam-containing environment.

Reactor temperatures were then brought up to 212°F temperature slowly over a period of 9 hrs and then held for about 1 hr before continuing to raise the temperature to about 392°F (200°C) over a period of 8 hrs. The unit was held at 392°F for about 2 hrs and then the heats turned off and the unit was allowed to cool to room temperature. On October 22nd the reactors were brought up to about 300°F in hydrogen on recycle and run feed was introduced.

Two slightly different sources of feed were hydrogenated in this program. One feed originated as virgin 1:1 RCO/LCO hydrotreated in the fall 2004 program while the other was a blend of jet fuel range product produced in programs conducted in earlier years.

(i) Hydrogenation of HDT+HDY 1:1 RCO/LCO Blends

The first feed to the hydrogenation reactor was the blend of 550°F- material from X-1099. The operating conditions and the daily GC analysis are shown in **Tables 1-2 and 1-3.**

Table 1-2

HYDROGENATION OF HYDROTREATED 1:1 RCO/LCO (Distilled to 550°F)

CATALYST		Engelhard REDAR (PC-76S)																								
CHARGE	ml	gm																								
Rx1	2251	1657																								
Rx2	2832	2084																								
T total	5083	3741																								
			Heats on:		12:00	8/13/04																				
			Start Run Feed:		13:45	10/22/04																				
NOMINAL RUN PRESSURE 1200 PSIG																										
Run No.	Time	Date	Tetralin Wt%	FEED RATE gms/hr	REACTOR 1				REACTOR 2				WABT COMB	LHSV	Inlet gas SCF/BL	Quench SCF/BL	Makeup SCF/BL	% H2 INLET	H ₂ Cons. SCF/BL	Wt Bal %	PRODUCT ANALYSES					
					IN	OUT	MAX	WABT	IN	OUT	MAX	WABT									S, PPM (l)	N, PPM (l)	Spec Grav gm/ml	5% F	95% F	% of 356°F.
					8HR AVG				8HR AVG												8HR AVG					
761	1345	10/22	4.24	Introduced 1st Pass Hydrog. Product (X-1099) Distilled to -550°F @ 200°F																4.6	2.4	0.8849	257	518	35.3	
762	2000	10/22		Increased the Inlet of Both Reactors to 225°F																						
763	2400	10/22		Increased the Inlet of Both Reactors to 250°F																						
764	0400	10/23		Increased the Inlet of Both Reactors to 275°F																						
764	0800	10/23	4.29	4361	274	276	276	274	275	283	283	280	277	1.15	3275	0	372	99.7	49	102.4	0.8833					
765	1100	10/23		Increased the Inlet of Both Reactors to 300°F																						
766	1500	10/23		Increased the Inlet of Both Reactors to 315°F																						
767	0400	10/24		Increased the Inlet of Both Reactors to 350°F																						
767	0800	10/24	0.13	4435	550	380	380	358	350	491	491	396	377	1.21	3065	0	876	99.6	592	99.4	3.6	0.98	0.8665	268	518	17.0
767	0800	10/24		On Stream Product DR #1 Properties																3.7	0.38	0.8750	270	529	15.0	
768	0900	10/24		Increased the Inlet of Reactor 1 to 365°F																						
769	1400	10/24		Decreased the Inlet of Reactor 2 to 325°F																						
769	0800	10/25	0.71	4441	365	418	418	382	326	460	460	401	392	0.99	3071	0	842	99.6	667	98.8	1.8	0.73	0.8628	273	520	15.6
769	2400	10/25	0.66	P67-76 Product DR #1 Properties (From X-1099 Feed)																1.5	0.01	0.8633	278	530	13.7	
769	0800	10/26	0.55	4512	364	400	400	376	325	479	479	414	395	1.00	3113	0	854	99.5	699	99.2	1.5	0.18	0.8607	278	529	14.0
769	0800	10/27	0.76	4350	366	382	382	370	324	461	461	400	385	0.99	3097	0	681	99.7	544	98.4	1.7	0.26	0.8639	276	527	13.6
769	1200	10/27	0.64	P67-76 Product DR #2 Properties (From X-1099 Feed)																1.3	0.68	0.8628	274	523	14.5	
769	0400	10/28	0.79	P67-76 Product DR #3 Properties (From X-1099 Feed)																2.0	0.74	0.8639	283	531	13.0	
771	0400	10/28	11.12	Changed Feed to X-1100 Blend																1.9	1.52	0.9053	322	524	9.9	
771	0800	10/28	0.41	4608	366	400	400	374	326	569	569	415	395	0.99	3001	0	1336	99.5	1206	97.6	2.3	0.40	0.8623	282	528	14.5
771	0800	10/29	0.39	4512	366	421	421	386	326	590	590	468	427	0.99	3381	0	1410	99.4	1232	98.3	1.2	0.36	0.8591	272	516	18.0
771	2000	10/29	0.46	P67-77 Product DR #1 Properties (From X-1100 Feed)																1.2	0.39	0.8602	271	518	18.0	
771	0400	10/30	0.27	4635	364	406	406	381	325	596	596	462	422	1.00	3004	0	1383	99.4	1247	99.1	1.0	0.03	0.8581	267	514	27.0
771	0400	10/31	0.25	4528	365	399	399	379	325	595	595	446	413	0.98	3084	0	1344	99.2	1184	98.7	1.2	0.06	0.8591	266	515	24.0
771	0800	10/31	0.44	P67-77 Product DR #2 Properties (From X-1100 Feed)																1.4	0.37	0.8602	272	518	17.5	
771	0400	11/1	0.48	4375	366	401	401	380	325	592	592	444	412	0.97	3062	0	1398	95.8	1196	98.5	1.4	0.75	0.8633	274	516	22.0
771	1400	11/1	0.47	P67-77 Product DR #3 Properties (From X-1100 Feed)																1.1	0.36	0.8571	276	519	17.0	
781	1400	11/1	21.27	Changed Feed to X-1101 Blend																1.3	1.31	0.9200	310	542	11.6	
781	0400	11/2	4.14	4568	366	411	411	381	326	636	636	462	422	0.99	3056	0	1596	99.4	1368	98.6	2.5	0.25	0.8724	291	511	16.5
781	0400	11/3	5.00	4511	366	427	427	387	326	602	602	442	415	0.98	3118	0	1434	99.6	1238	97.4	1.7	0.82	0.8783	304	510	13.7
781	0400	11/3	4.22	P67-78 Product DR #1 Properties (From X-1101 Feed)																1.2	0.51	0.8724	291	510	16.5	
782	0900	11/3		Decreased the LHSV to 0.6																						
782	0400	11/4	0.24	2644	366	708	708	460	324	400	400	412	436	0.60	3110	0	2482	99.7	2008	98.3	0.8	0.59	0.8529	253	491	26.0
783	0900	11/4		Increased the LHSV to 0.75																						
783	0400	11/5	0.23	3468	365	644	644	442	324	442	442	394	418	0.75	2990	0	2152	99.5	1857	99.2	0.9	0.18	0.8633	304	508	13.0
783	0400	11/5	0.91	P67-78 Product DR #2 Properties (From X-1101 Feed)																1.8	0.33	0.8612	282	506	15.7	
784	2300	11/5		Changed feed to P67-78 Product DR #1 and increased the LHSV to 1.0																						
784	0400	11/6	0.33	4111	362	420	420	407	321	424	424	378	393	1.00	3168	0	915	99.5	705	98.2	1.6	0.97	0.8644	297	504	15.0
784	2400	11/6	0.31	P67-78 Product DR #3 Properties (From X-1101 Feed)																2.0	0.17	0.8633	298	503	14.6	
784	0400	11/7	0.33	4393	366	401	401	376	326	396	396	353	365	1.00	3014	0	752	99.8	495	98.0	1.7	0.65	0.8639	295	501	16.0
784	1500	11/7	0.37	P67-78 Product DR #4 Properties (From P67-78 Product DR #1 as Feed)																						
				SR-0225 (P67 -76 thru 78 Distilled Jet Fuel Product (356°F to 518°F))																0.7	0.70	0.8713	343	520	8.0	

Table 1-3

DAILY GC ANALYSES OF HYDROGENATED TLP PRODUCTS (Product: SR-0225)

Column: 150 meterx0.25mm, Supelco DH 150 Petrolal

FID Film Thickness 1 micron

United Refining LCO - RCO Hydrotreating

GC No.	SAMPLE	Benz	Cydo Hexane	Et B	Xyfs	Indan (I)	t-Dec	e-Dec	Tetralin	N	MNS		EtN's	DMNS								TOTAL DMN's	TOTAL MNS	Tri-	Tetra	5+6	Other
											2MN	1MN		2,6	2,7	1,7	1,6	2,3	1,5	1,2	1,8						
3030	P67-76 TLP 10/23/04	0,10	1,03		0,73	0,41	20,80	5,33	4,29	0,63	0,65	0,73	0,43	0,21	0,15	0,22	0,37	0,62	0,67	0,15	0,11	2,50	1,38	1,86	0,84		92,79
3034	P67-76 TLP 10/24/04		1,11		0,16	0,03	26,42	5,09	0,13	0,98	0,31	1,04	0,51	0,12	0,07	0,11	0,29	0,17	0,18	0,08	0,06	1,08	1,35	1,26	0,67		94,66
3038	P67-76 TLP 10/25/04		1,44		0,17	0,18	26,37	6,72	0,71	0,99	0,38	1,15	0,55	0,15		0,09	0,27	0,12	0,15	0,06	0,08	0,92	1,53	1,42		95,14	
3044	P67-76 TLP 10/26/04		1,41		0,16	0,17	27,60	5,67	0,55	0,94	0,27	1,10	0,52	0,14		0,090	0,26	0,14	0,15	0,06	0,04	0,88	1,37	1,13	1,08		94,60
3050	P67-76 TLP 10/27/04		1,22		0,19	0,18	25,66	7,13	0,76	0,95	0,28	1,12	0,54	0,10	0,04	0,09	0,27	0,11	0,14	0,05	0,03	0,83	1,40	1,06	0,94		94,82
3053	P67-77 TLP 10/28/04		1,16		0,14	0,27	26,38	3,63	0,41	1,17	0,38	0,50	0,47	0,09	0,10	0,13	0,24	0,17	0,17	0,16	0,11	1,17	0,88	0,61	0,15		96,02
3057	P67-77 TLP 10/29/04		1,08		0,15	0,34	26,62	3,44	0,39	1,22	0,36	0,40	0,42	0,07	0,08	0,10	0,16	0,13	0,13	0,11	0,05	0,83	0,76	1,03	0,79		95,37
3061	P67-77 TLP 10/30/04		0,81		0,15	0,31	24,72	3,64	0,27	1,13	0,37	0,49	0,51	0,18	0,10	0,12	0,27	0,17	0,20	0,10	0,07	1,21	0,86	0,94	0,01		95,85
3062	P67-77 TLP 10/31/04		0,48		0,08	0,09	25,20	4,14	0,25	0,88	0,17	0,29	0,54	0,17	0,10	0,15	0,28	0,15	0,11	0,19	0,07	1,22	0,46	0,93	0,35		96,16
3064	P67-77 TLP 11/1/04		1,10		0,14	0,24	26,59	4,46	0,48	1,14	0,32	0,56	0,50	0,08	0,07	0,10	0,22	0,14	0,14	0,11	0,03	0,89	0,88	0,87	0,78		95,44
3072	P67-78 TLP 11/2/04		0,94		0,31	0,27	22,18	5,48	4,14	0,95	0,15	0,83	0,70	0,16	0,12	0,25	0,29	0,42	0,58	0,11	0,14	2,07	0,98	0,90		95,10	
3074	P67-78 TLP 11/3/04		0,80		0,33	0,14	23,30	5,91	5,00	0,93	0,14	0,95	0,80	0,07	0,13	0,29	0,38	0,48	0,72	0,13	0,19	2,39	1,09	0,89		94,70	
3079	P67-78 TLP 11/4/04		1,21		0,26	0,52	24,37	4,10	0,25	0,94	0,34	0,52	0,38	0,20	0,06	0,06	0,18	0,07	0,10	0,08	0,05	0,80	0,86	0,20		97,20	
3082	P67-78 TLP 11/5/04		1,01		0,16	0,21	29,85	5,06	0,23	1,13	0,30	0,22	0,64	0,06	0,09	0,11	0,30	0,08	0,11	0,05	0,04	0,84	0,52	0,36		97,15	
3085	P67-78 TLP 11/6/04		0,68		0,16	0,26	26,07	6,95	0,33	1,10	0,3	0,23	0,72	0,11	0,06	0,14	0,31	0,12	0,07	0,06	0,04	0,91	0,53	0,36		97,10	
3086	P67-78 TLP 11/7/04		1,14		0,18	0,29	28,29	7,53	0,33	1,10	0,27	0,19	0,57	0,11		0,10	0,20	0,12	0,03			0,56	0,46	0,23	0,71		96,94

After the previous hydrogenation runs this blend still contained 4.2 wt% tetralin 4.6 ppm sulfur, 2.4 ppm nitrogen and had a specific gravity of between 0.8849 and 0.9200. After the run feed was introduced at 1 LHSV Reactor 1 established a delta T of about 50°F and Reactor 2 had about 35°F. Hydrogenation product had 1-2 ppm sulfur and <1 ppm nitrogen and a specific gravity of 0.8633. This further hydrogenation removed the remaining tetralin to <1 wt% as shown in **Table 1-4**.

Table 1-4

GC ANALYSES OF FEEDS and HYDROGENATED TLP PRODUCTS (Product: SR-0225)

Column: 150 meter x 0.25mm, Supelco DB150 Retocul

FID Film Thickness 1 micron

United Refining LCO - RCO Hydrotreating

GC No.	SAMPLE	Benz	Cyclo Hexane	EIB	Xyfs	Indan (I)	tDec	c-Dec	Tetralin	N	MNS		Ecn's	DMN'S								TOTAL	TOTAL	Tri-	Tetra	5+6	Other
											2MN	1MN		2,6	2,7	1,7	1,6	2,3	1,5	1,2	1,8	DMN's	MNS	MeSubstMN's			
3023	FEED 4X-1099 Blend)	0.12	1.31		0.76	0.43	21.45	5.41	4.24	0.9	0.33	0.69	0.83	0.25	0.25	0.26	0.42	0.60	0.62	0.13	0.10	2.63	1.02	2.94	0.41		92.10
3041	OilStream prod. DR #1	0.06	1.39		0.46	0.23	23.38	6.21	2.26	0.80	0.45	0.91	0.46		0.29	0.18	0.32	0.31	0.45	0.21	0.08	1.84	1.36	1.33	1.14		93.07
3043	P67-76 Product Drum #1		1.24		0.17	0.16	25.63	6.30	0.66	0.96	0.29	1.11	0.56	0.12	0.31	0.11	0.31	0.15	0.17	0.08	0.07	1.32	1.40	1.23	0.79		93.74
3051	P67-76 Product Drum #2		1.15		0.17	0.16	26.37	5.99	0.64	0.97	0.29	1.12	0.55	0.06	0.11	0.10	0.29	0.15	0.17	0.07	0.06	1.01	1.41	1.41	0.24		94.41
3054	P67-76 Product Drum #3		1.18		0.19	0.17	25.98	7.42	0.79	0.96	0.28	1.12	0.55	0.10	0.04	0.09	0.27	0.11	0.14	0.05	0.03	0.83	1.40	1.21	0.17		95.43
3058	FEED 4X-1100 Blend)	0.13	0.91		1.01	1.02	17.19	4.36	11.12	0.97	0.34	1.98	1.72	0.27	0.29	0.28	0.50	0.69	1.01	0.10	0.26	3.40	2.32	2.03	0.26		91.02
3065	P67-77 Product Drum #1		1.08		0.15	0.34	26.14	3.52	0.40	1.19	0.37	0.44	0.45	0.08	0.10	0.12	0.21	0.16	0.16	0.15	0.05	1.03	0.81	0.64	0.13		96.20
3066	P67-77 Product Drum #2		1.15		0.11	0.32	26.82	4.00	0.44	1.19	0.35	0.48	0.45	0.07	0.08	0.08	0.18	0.14	0.16	0.11	0.03	0.85	0.83	1.00	0.14		95.99
3070	P67-77 Product Drum #3		1.09		0.13	0.25	27.02	4.46	0.47	1.15	0.32	0.55	0.50	0.07	0.13	0.10	0.21	0.13	0.13	0.11	0.03	0.91	0.87	0.88	0.69		95.50
3059	FEED 4X-1101 Blend)	0.08	0.97		1.13	1.77	11.58	3.61	21.27	1.12	1.34	2.61	2.15	0.29	0.32	0.29	0.61	0.82	1.63	0.11	0.50	4.57	3.95	1.51			88.85
3075	P67-78 Product Drum #1	0.02	0.85		0.32	0.24	22.52	5.52	4.22	0.95	0.15	0.86	0.73	0.16	0.13	0.26	0.30	0.43	0.60	0.12	0.15	2.15	1.01	0.79			95.10
3083	P67-78 Product Drum #2		1.09		0.21	0.31	26.40	5.00	0.91	1.02	0.24	0.19	0.59	0.13	0.07	0.13	0.27	0.12	0.21	0.12	0.05	1.10	0.43	0.47			96.98
3089	P67-78 Product Drum #3		0.79		0.16	0.24	27.50	6.27	0.31	1.16	0.31	0.23	0.68	0.06	0.10	0.13	0.31	0.12	0.06	0.06	0.03	0.87	0.54	0.47			96.96
3090	P67-78 Product Drum #4		0.79		0.17	0.28	27.24	7.38	0.37	1.05	0.28	1.10	0.67	0.05	0.09	0.12	0.28	0.17	0.05	0.05	0.03	0.84	1.38	0.37	0.45		95.91
3101	SR-0225 (P67-76/78)		0.50		0.04	0.24	29.33	5.97	0.41	1.21	0.36	1.05	0.59	0.06	0.11	0.11	0.26	0.11	0.09	0.06	0.03	0.83	1.41	0.79	0.64		95.12

The next blend, X-1100, was introduced to the unit without interruption or change to the reactor temperatures. Due to the higher tetralin in this blend 11.1 wt%, the delta T increased slightly to about 80°F in the first reactor and about 55°F in the second reactor. Each of the three product drums had <1 wt% tetralin after one pass.

The final blend, X-1101, from the previous hydrogenation runs was also added to the unit with no interruptions. With 21.3 wt% tetralin this blend contained the highest tetralin of the three blends, however, the delta T did not increase. This was evident in the 4 wt% tetralin still in the product. After the first product drum was made the LHSV was reduced to 0.75. After this change the remaining two product drums had tetralin amounts of <1wt%. The first product drum was then double passed and had a tetralin value of <1 wt%. The components with their boiling points of both the raw feed and the hydrogenated product are shown in **Table 1-5**.

Table 1-5

BOILING POINTS OF SOME RAW FEED AND JP-900 COMPONENTS								
Component in Raw Material----->				Hydrogenated Component----->				Delta
	wt %	Bpt, C	Bpt, F		wt %	Bpt, C	Bpt, F	Bpt, F
benzene	0,3	80,1	176,2	cyclohexane	0,5	80,7	177,3	-1,1
toluene		110,6	231,1	Me-cyclohexane		100,9	213,6	17,5
p-xylene		138,3	280,9	t-1,4-DiMe-cyclohexane		119,4	246,9	34,0
				c-1,4-DiMe-cyclohexane		124,3	255,7	25,2
m-xylene		139,1	282,4	t-1,3-DiMe-cyclohexane		124,5	256,1	26,3
				c-1,3-DiMe-cyclohexane		120,1	248,2	34,2
o-xylene		144,4	291,9	t-1,2diMe-cyclohexane		123,4	254,1	37,8
Total Xylenes	0,5			c-1,2-DiMe-cyclohexane		129,7	265,5	26,5
Indene	2	182,6	360,0	Indan(Dihydroindene)	0,3	178,0	350,0	10,0
				Octahydroindene		?		
naphthalene	31	218	424,4	trans-decalin	29-38	187,3	369,1	55,4
				cis-decalin	5-6	195,7	384,2	40,2
				tetralin	0.5-3	207,6	405,6	18,8
1-methylnaphthalene	1,8	244,6	472,3	1-methyldecalin (trans)		?	432 est	
2-methylnaphthalene	0,1	241,1	465,9	2-methyldecalin (trans)		?	416 est	
1,2 DMN		266,5	511,7			?		
1,3 DMN		263	505,4			?		
1,4 DMN		268	514,4			?		
1,5 DMN		265	509,0			?		
1,6-DMN		264	507,2			?		
1,7-DMN		263	505,4			?		
1,8-DMN		270	518,0			?		
2,3-DMN		268	514,4			?		
Total DMN's	8,3		505-518				465-478 est	
Trimethylnaphthalenes	2,8	264	507,2			?	467 est	
Acenaphthene	1,5	279	534,2			?		
Phenanthrene	1,3	340	644,0			?		
Carbazole	0,1	355	671,0	1,2,3,4-tetrahydrocarbazole		330,0	626,0	45,0

Distillation of hydrogenated products

There were a total of nine drums (380 gallons) of feed processed. These drums were then sent to the stillroom to distill the gasoline fraction from the jet fuel fraction. The 150-still was used to distill the nine product drums. The products were distilled immediately after each set of drums came off of P67.

Three cuts were taken on the first distillation (X-1103) based on wanting the 5% point on the simulated distillation at 356°F. The product was cut at 346, 356 and 366°F to produce the three cuts plus the bottoms fraction. Cuts 356 and 366°F were mainly comprised of 356°F+ material and were then blended back with the jet fuel fraction. The 346°F cut did not produce a clean cut and therefore it was added to the second distillation for better separation.

The second and third distillations (X-1104 and X-1106) each had four cuts still based on the 356°F point at 5%. The cuts were 310, 320, 330 and 340°F. These cuts allowed for better separation of the gasoline and the jet fuel products. In X-1104 cuts 310 and 320°F were kept as gasoline and the remaining two cuts were blended with the jet fuel. In the X-1106 distillation the cuts were slightly better, therefore the first three cuts were kept as gasoline.

550°F+ distillation

The bottoms from the three 150-gallon Still feed distillations were combined in PARC's Fractioneer still to separate the diesel fuel and the fuel oil. There was a total of

47 gallons of material but only 42 gallons of material was charged to the still. The other 5 gallons of 550°F+ bottoms were retained if needed for future use. The distillation resulted in an almost 1:1 split of diesel fuel and fuel oil. The Fractioneer produced 21.8 gallons of diesel fuel. This was combined with the 33.1 gallons of diesel fuel cuts that were left out of both the P67 feed (550°F-) and the Fractioneer. This resulted in a total of 54.9 gallons of diesel fuel produced. There was a total of 20.2 gallons of fuel oil from the Fractioneer run.

(ii) Hydrogenation of HDT jet fuel range material (1st pass)

The second feed was a composite of jet fuel fractions from hydrotreating programs conducted in years prior to 2004. The blend was made of 221 gallons of jet fuel range material derived from 1:1 RCO/LCO labeled as SR-0224. Only 142 gallons of jet fuel was needed to complete the 500 gallons required for the project. Since SR-0224 was already jet fuel range material and it was not necessary to distill the feed, this was enough material to complete the project. This feed had a sulfur and nitrogen concentration of 17.2 and 198.4 ppm respectively. This high concentration of nitrogen proved problematic with the catalyst and extended the time to process the material.

SR-0224 went into the unit on November 11th immediately following the end of the X-1101 feed. Due to the high levels of naphthalene and tetralin in the feed, the reactor inlet temperatures were reduced to 300°F. This was done to keep the outlet of the reactors below 600°F since in previous hydrogenation runs using hydrotreated feeds delta T's of 300°F were observed. However, very little reaction occurred at 300°F. The inlet

temperatures for the two reactors were slowly increased to 450 and 375°F respectively. At these reactor inlet temperatures 600°F reactor outlet temperature was achieved. This was all done within the first 24 hours of this run.

Slowly throughout the run the inlet temperatures had to be increased in order to keep the outlet of each reactor at 600°F. The operating conditions and the daily GC analysis are shown in **Tables 1-6 and 1-7**, reveals that approximately 88% of the nitrogen in the feed was removed in the process. The nitrogen in the feed is removed and stays on the catalyst reducing its active sites and the catalyst's activity. Throughout the first pass the outlet temperatures were held at 600°F and the tetralin levels slowly decreased from 27 wt% in the first product drum to 22 wt% in the fourth product drum. A second pass was needed to reduce the concentration of tetralin to approximately 1 wt% tetralin or less in order for the jet fuel to pass the smoke point test.

CATALYST		Engelhard REDAR (PC-766)																																
CHARGE		ml	gm																															
	Rx1	2251	1657																															
	Rx2	2832	2084																															
	Total	5083	3741																															
				Heats on:		12:00	8/13/04																											
				Start Run Feed:		13:45	10/22/04																											
														NOMINAL RUN PRESSURE 1200 PSIG																				
Run	Time	Date	TetraIn	FEED	REACTOR 1				REACTOR 2				WABT	LHSV	Inletgs	Quench	Makeup	% H2	H ₂ Cons.	Wt Bal	PRODUCT ANALYSES													
No.			Wt%	RATE	IN	OUT	MAX	WABT	IN	OUT	MAX	WABT	COMB		SCF/B.L	SCF/B.L	SCF/B.L	INLET		%	S.PPM	N.PPM	Spec Grav	5%	95%	% of								
P-67				gm/hr	8HR AVG				8HR AVG				8HR AVG				8HR AVG				8HR AVG				(I)	(I)	gm/ml	F	F	350°F				
791	1500	11/7	32.24	Changed feed to SR-0224																				17.2	198.43	0.9462	348	518	5.8					
792	2000	11/7		Increased Rx1 In let to 335°F and decreased Rx2 In let to 300°F																														
792	0400	11/8	31.71	2419	326	390	390	353	320	572	572	425	389	0.50	4146	0	2143	99.7	1408	103.8	6.4	88.18	0.9082	346	514	6.0								
793	0800	11/8		Increased Rx1 Inlet to 330°F and Increased Rx2 Inlet to 325°F																														
794	1100	11/8		Increased Rx1 Inlet to 365°F and Increased Rx2 Inlet to 335°F																														
795	1300	11/8		Increased Rx1 Inlet to 380°F																														
796	1600	11/8		Increased Rx1 Inlet to 480°F																														
796	0400	11/9	20.74	2436	480	473	551	482	333	339	339	337	410	0.51	3960	1108	2459	99.8	1853	97.6	11.1	29.87	0.9013	346	511	6.5								
797	1000	11/9		Decreased Rx1 to 49°F																														
798	2200	11/9		Found quench valve plugged																														
798	0400	11/10	40.32	2403	414	427	453	418	372	377	380	374	396	0.50	3605	decreasing	2348	99.8	1743	96.7	7.3	120.68	0.9285	344	513	6.5								
798	1600	11/10	27.03	P67-79 Product DR#1 Properties (From SR0231 Feed)																				4.1	78.84	0.9111	348	510	7.8					
798	0400	11/11	11.52	2473	442	573	573	499	358	677	677	467	483	0.51	4035	0	2609	99.9	1907	100.4	2.8	5.23	0.8877	337	507	8.0								
798	0800	11/12	21.91	2460	454	397	397	510	425	539	539	473	492	0.52	3953	0	2648	99.9	1838	93.8	1.6	24.56	0.9047	348	513	6.5								
798	0400	11/13	20.05	2891	454	596	596	513	428	618	618	493	503	0.50	3761	0	3060	99.8	2272	97.3	1.5	15.08	0.8996	350	512	5.8								
798	2000	11/13		P67-79 Product DR#2 Properties (From SR0234 Feed)																				1.8	25.66	0.9082	352	513	5.6					
798	0400	11/14	24.27	2448	459	611	611	516	439	550	550	477	497	0.51	3856	0	1982	99.7	1193	99.1	1.6	28.30	0.9059	351	514	5.6								
798	0400	11/15	11.30	2433	461	604	604	518	436	693	693	534	526	0.50	3868	0	2578	99.6	1847	99.2	1.2	4.39	0.8871	339	510	7.7								
798	0400	11/16	20.25	2326	465	574	574	507	433	581	594	504	506	0.49	4072	0	1987	99.8	1169	99.2	2.5	41.52	0.9117	350	515	5.6								

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Table 1-7

DAILY GC ANALYSES OF HYDROGENATED TLP PRODUCTS (Product: SR-0226)

Column: 150 meter x 0.25mm, Supelco DB150 Peltocal

FID Film Thickness 1 micron

United Refining LCO - RCO Hydrotreating

GC No.	SAMPLE	Benz	Cyclo Hexane	EtB	Xyfs	Indan (I)	tDec	cDec	Tetralin	N	MNS		EtN's	DMN's								TOTAL	TOTAL	Tri-	Tetra	5+6	Other
											2MN	1MN		2,6	2,7	1,7	1,6	2,3	1,5	1,2	1,8	DMN's	MNS	MeSubstMN's			
3080	SR-0224		0.38		0.26	2.63	2.47	0.89	32.24	10.8	1.87	0.92	0.83	0.58	0.59	1.14	0.84	0.69	0.86	0.22	0.54	5.46	2.79	1.44	0.17		79.38
3088	P67-79 TLP 11/8/04		0.43		0.14	1.87	9.20	3.06	31.71	1.38	0.13	0.17	0.83	0.21	0.21	0.20	0.47	0.50	0.77	0.07	0.43	2.86	0.30	0.67	0.18		94.61
3092	P67-79 TLP 11/9/04		0.44		0.14	1.25	18.32	6.75	20.74	0.64	1.17	0.18	0.81	0.07	0.11	0.20	0.34	0.39	0.63	0.11	0.31	2.16	1.35	0.60			95.25
3095	P67-79 TLP 11/10/04		0.43		0.07	2.50	4.42	1.66	40.31	0.28	0.11	0.27	0.82	0.07	0.13	0.20	0.44	0.51	0.86	0.15	0.48	2.84	0.38	0.70	0.34	0.00	95.46
3097	P67-79 TLP 11/11/04		0.60		0.11	0.73	25.78	5.79	11.52	0.98	0.09	0.13	0.73	0.15	0.14	0.09	0.31	0.33	0.47	0.10	0.18	1.77	0.22	0.70	0.03		96.30
3100	P67-79 TLP 11/12/04		0.51		0.14	1.32	19.35	4.97	21.91	0.55	1.24	0.15	1.52	0.06	0.12	0.22	0.40	0.42	0.73	0.11	0.31	2.37	1.39	0.68	0.12		94.89
3105	P67-79 TLP 11/13/04		0.44		0.13	1.20	20.94	5.10	20.05	0.61	1.16	0.86	1.44	0.06	0.11	0.22	0.39	0.40	0.70	0.11	0.30	2.29	2.02	0.39	0.19		94.50
3104	P67-79 TLP 11/14/04		0.39		0.13	1.47	17.59	4.53	24.27	0.51	1.33	0.80	1.59	0.06	0.12	0.22	0.41	0.43	0.76	0.10	0.33	2.43	2.39	0.41	0.13		93.31
3103	P67-79 TLP 11/15/04		0.55		0.13	0.72	25.84	5.73	11.30	1.00	0.09	0.82	0.69	0.14	0.12	0.16	0.29	0.31	0.47	0.08	0.17	1.74	0.91	0.40	1.08		94.87
3108	P67-79 TLP 11/16/04		0.37		0.14	1.71	13.45	3.32	29.25	0.41	1.54	0.60	1.71	0.07	0.13	0.21	0.45	0.47	0.81	0.12	0.40	2.66	2.14	0.57	0.14		94.08
3110	P67-79 TLP 11/17/04		0.35		0.14	1.55	14.74	3.57	26.28	0.46	1.42	0.69	1.63	0.07	0.13	0.22	0.44	0.45	0.77	0.12	0.37	2.57	2.11	0.65	0.23		93.98
3113	P67-79 TLP 11/18/04		0.60		0.14	1.07	20.76	4.76	18.59	0.72	1.14	0.78	1.39	0.07	0.13	0.22	0.35	0.39	0.65	0.11	0.28	2.20	1.92	0.61	0.11		94.44
3115	P67-79 TLP 11/19/04		0.58		0.15	1.43	17.29	3.99	24.78	0.51	1.35	0.14	1.58	0.06	0.12	0.21	0.42	0.43	0.76	0.11	0.36	2.47	1.49	0.63	0.09		94.81
3118	P67-79 TLP 11/20/04		0.40		0.14	1.43	16.44	3.75	24.73	0.51	1.37	0.68	1.58	0.07	0.13	0.21	0.42	0.43	0.75	0.11	0.35	2.47	2.05	0.69	0.11		94.17
3117	P67-79 TLP 11/21/04		0.38		0.10	1.14	21.03	4.67	20.20	0.58	1.17	0.17	1.41	0.06	0.11	0.20	0.39	0.40	0.68	0.11	0.31	2.26	1.34	0.65	0.17		95.00
3120	P67-80 TLP 11/22/04		0.45		0.14	0.65	27.53	6.30	10.92	0.78	0.77	0.10	1.10	0.13	0.11	0.22	0.33	0.33	0.57	0.10	0.20	1.99	0.87	0.59			95.77
3126	P67-80 TLP 11/23/04		0.52		0.09	0.13	35.35	7.46	1.87	1.08	0.11	0.14	0.59	0.08	0.05	0.13	0.16	0.15	0.21	0.05	0.04	0.87	0.25	0.28			97.52
3128	P67-80 TLP 11/24/04		0.61		0.09	0.16	37.22	6.77	0.26	1.14	0.23	0.17	0.58	0.13			0.21	0.04	0.05	0.04	0.04	0.51	0.40	0.25	0.10		97.60
3131	P67-80 TLP 11/25/04		0.41		0.09	0.14	38.64	5.00	0.18	1.18	0.24	0.18	0.56	0.10	0.05	0.07	0.15	0.07	0.07	0.07	0.04	0.62	0.42	0.32	0.08		97.38
3134	P67-80 TLP 11/26/04		0.41		0.08	0.13	39.30	4.85	0.18	1.21	0.25	0.18	0.50	0.05	0.09	0.07	0.15	0.07	0.07	0.06	0.04	0.60	0.43	0.24	0.10		97.42
3137	P67-80 TLP 11/27/04		0.42		0.08	0.13	38.08	5.41	0.18	1.18	0.26	0.18	0.56	0.05	0.10	0.07	0.16	0.07	0.07	0.07	0.04	0.63	0.44	0.18	0.43		97.14
3147	P67-80 TLP 11/2/04		0.43		0.08	0.11	39.39	5.70	0.15	1.18	0.20	1.51	0.59	0.06		0.07		0.07	0.07	0.06	0.04	0.37	1.71	0.21	0.26		96.27
3143	P67-80 TLP 11/29/04		0.53		0.08	0.11	39.20	5.68	0.16	1.19	0.21	1.48	0.59	0.13	0.00	0.07	0.07	0.07	0.07	0.06	0.03	0.50	1.69	0.19			96.43
3149	P67-80 TLP 11/30/04		0.45		0.08	0.11	38.98	5.16	0.16	1.19	0.23	1.51	0.60	0.15		0.07	0.17	0.08	0.07	0.06	0.06	0.66	1.74	0.18			96.23
3163	P67-80 TLP 12/1/04		0.46		0.08	0.12	39.59	4.96	0.18	1.23	0.28	1.19	0.46	0.09	0.04	0.06	0.15	0.07	0.06	0.05	0.03	0.55	1.47	0.21	0.10		96.44
3176	P67-80 TLP 12/2/04		0.43		0.08	0.13	37.88	6.27	0.23	1.16	0.23	1.39	0.59	0.05	0.10	0.06	0.18	0.07	0.06	0.07	0.03	0.62	1.62	0.20	0.12		96.28
3180	P67-80 TLP 12/3/04		0.51		0.08	0.12	38.79	6.04	0.23	1.18	0.24	1.35	0.54	0.13		0.05	0.15	0.06	0.04	0.05	0.05	0.53	1.59	0.17	0.19		96.34
3187	P67-80 TLP 12/4/04		0.48		0.09	0.13	38.55	6.11	0.23	1.18	0.24	1.36	0.55	0.08		0.05	0.15	0.06	0.04	0.05	0.05	0.48	1.60	0.11			96.63
3185	P67-80 TLP 12/5/04		0.50		0.09	0.14	36.02	7.07	1.43	1.10	0.11	1.29	0.60	0.08	0.05	0.11	0.18	0.15	0.18	0.05	0.04	0.84	1.40	0.26	0.30		96.10
3184	P67-80 TLP 12/6/04		0.57		0.09	0.15	34.49	6.94	1.69	1.07	0.12	1.25	0.62	0.11	0.07	0.13	0.21	0.18	0.21	0.07	0.06	1.04	1.37	0.24	0.12		96.16
3189	P67-80 TLP 12/7/04		0.56		0.14	0.14	37.75	6.37	0.28	1.16	0.25	1.30	0.55	0.12			0.21	0.06	0.08	0.04	0.05	0.56	1.55	0.23	0.10		96.40

(iii) Hydrogenation of HDT jet fuel range material (2nd pass)

The second pass started on November 20th with the first product drum. This feed had <1 wt% naphthalene and 27 wt% tetralin. The first and second reactor inlet temperatures at the start of the second pass were 486°F and 422°F respectively. There was an initial exotherm of 40°F on the first reactor and an 80°F exotherm on the second reactor. After two days of running the first product drum was finished with a tetralin level of 16.4 wt%. This product drum was a composite of both 1st and 2nd pass product. This product drum was sent through again once the other product drums were re-passed. The product drums GC analysis of both passes are shown in **Table 1-8**.

Table 1-8

GC ANALYSES OF FEEDS and HYDROGENATED TLP PRODUCTS (Product: SR-0226)

Column: 150 meter x 0.25mm, Supelco DB150 Rt/coul

FID Film Thickness 1 micron

United Refining LCO - RCO Hydrotreating

GC No.	SAMPLE	Benz	Cyclo Hexane	EtB	Xyfs	Indan (I)	tDec	c-Dec	Tetralin	N	MNS		EN%	DMN'S								TOTAL	TOTAL	Tri-	Tetra	5+6	Other
											2MN	1MN		2,6	2,7	1,7	1,6	2,3	1,5	1,2	1,8	DMN's	MNS	MeSubstMN's			
3080	FEED (SR-0224)		0.38		0.26	2.63	2.47	0.89	32.24	10.76	1.87	0.92	1.89	0.58	0.59	1.14	0.84	0.69	0.86	0.22	0.54	5.46	2.79	1.44	0.17		79.38
3098	P67-79 Product Drum #1		0.53		0.18	1.63	14.04	4.04	27.03	0.85	1.51	0.08	1.42	0.14	0.14	0.07	0.38	0.43	0.69	0.14	0.35	2.34	1.59	0.66	0.08		94.48
3106	P67-79 Product Drum #2		0.45		0.13	1.44	17.47	4.58	23.93	0.54	1.32	0.78	1.57	0.06	0.12	0.22	0.42	0.43	0.75	0.11	0.34	2.45	2.10	0.40	0.10		94.41
3111	P67-79 Product Drum #3		0.45		0.13	1.31	18.30	4.42	21.90	0.63	1.26	0.79	1.50	0.07	0.13	0.23	0.37	0.42	0.71	0.11	0.32	2.36	2.05	0.62			94.34
3121	P67-79 Product Drum #4		0.41		0.13	1.29	18.46	4.33	21.96	0.57	1.26	0.06	1.52	0.07	0.13	0.22	0.42	0.42	0.72	0.13	0.32	2.43	1.32	0.63	0.05		95.00
3124	P67-79 Product Drum #5		0.36		0.10	0.97	22.72	5.27	16.44	0.66	1.01	0.08	0.79	0.06	0.11	0.21	0.37	0.37	0.62	0.11	0.26	2.11	1.09	0.65	0.08		95.41
	<i>Start of 2nd Pass Product</i>																										
3145	P67-79 Product Drum #6		0.63		0.09	0.16	39.57	6.24	0.62	1.19	0.14	1.28	0.51	0.08				0.08	0.08	0.04	0.03	0.31	1.42	0.17			96.91
3146	P67-79 Product Drum #7		0.43		0.08	0.13	39.24	5.40	0.19	1.19	0.22	1.42	0.56	0.09		0.06		0.07	0.06	0.06	0.04	0.38	1.64	0.20	0.07		96.52
3178	P67-79 Product Drum #8		0.53		0.08	0.12	39.49	5.59	0.19	1.20	0.23	1.40	0.55	0.12		0.06	0.16		0.06	0.04	0.04	0.48	1.63	0.17	0.23		96.29
3186	P67-79 Product Drum #9		0.58		0.09	0.14	38.50	6.46	0.49	1.17	0.16	1.36	0.56	0.11			0.20	0.09	0.08	0.03	0.04	0.55	1.52	0.17	0.10		96.49
3190	P67-79 Product Drum #10		0.55		0.08	0.15	36.40	6.83	1.05	1.12	0.13	1.27	0.59	0.09	0.05	0.10	0.15	0.13	0.15	0.06	0.03	0.76	1.40	0.33			96.39

Through out the second pass the first reactor remained lined out with an inlet temperature of 488°F and an outlet temperature around 600°F. The second reactor saw slight variations in both the inlet and outlet temperatures but overall remained around 450°F and 580°F respectively. All of the product drums all had less than 1 wt % tetralin and naphthalene except for the 10th drum which had 1.05 wt% tetralin. Once the run was complete it was decided that the product did not need to be distilled because the feed was previously hydrotreated and distilled to the 356°F to 518°F range for the jet fuel fraction. The product drums were blended together and labeled, SR-0226.

(C) Clay treatment of jet fuel

The jet fuel was in two separate blends identified as SR-0225 and SR-0226. These blends had different compositions presumably due to differing amounts of naphthalene in each virgin feed. Because of the difference in the feedstocks the final concentration of decalin in the blend SR-0226 was approximately 10 wt% higher than that of SR-0225. Since both blends were needed to make-up the 10 drums of jet fuel, it was decided that the two blends would be composited into one final blend identified as SR-0227. This blend had a final decalin concentration of 38 wt%.

Tests were done, as part of our AFOSR program, to determine if treating the jet fuel over activated clay would lower the amount of carbon in the stability test. This test measures the amount of carbon (mg) per cm². A lower carbon number is beneficial due to less build up of carbon deposits. Engelhard F-24 clay was used for this test. During the clay treat tests it was determined that the jet fuel went from a carbon number of 7.62

mg/cm³ to 1.63 mg/cm³. Due to this decrease in carbon deposits it was decided to clay treat the jet fuel blend.

The jet fuel was treated in a 36" glass column. The column was filled with the Engelhard F-24 clay based on a one drum per charge basis. The amount of clay needed to treat each drum depended on the amount of jet fuel in the drum. PSU determined the clay to jet fuel ratio in small-scale tests. For every 15.7 lbs of jet fuel being treated, one pound of clay was needed. Once the column was filled with clay the jet fuel was pressured into the column with nitrogen. There was a vent on the top of the column to allow the jet fuel to gravity flow through the clay. Once the jet fuel passed over the clay it drained straight into a 55-gallon drum and ready to be shipped. This 55-gallon drum was continuously purged while being filled with the jet fuel.

There were a total of 10 full 55-gallon drums and 1 partial 55-gallon drum that was treated through the F-24 clay. The treatment took a total of 7 days to treat, which averaged to be 1½ drums of jet fuel treated per day.

The description of proof of performance of the jet fuel (the work done as part of our AFOSR program), even though not a part of this program, validates that the gasoline, diesel and fuel oil co-produced with the jet fuel represents useful materials that, in fact, would be co-produced with a jet fuel having similar properties and performance in a refinery run.

(D) Overall production flow scheme

The product flow diagram is shown in **Figure 1-2**. This figure shows the steps and products made during the process.

The composition of the feed and jet fuel product at different stages in the process is shown in **Table 1-9**. The yields and analysis for all of the different products made are shown in **Table 1-10**. A comparison of the products (SR-0225, SR-0226, SR-0227 and SR-0227 clay treated), military specifications and commercial samples of JP-5 and JP-8 is shown in **Table 1-11**.

Table 1-9

FEED AND PRODUCT COMPOSITION AT DIFFERENT STAGES							
Material	Naphthalene	Tetralin	Trans-Decalin	Cis-Decalin	Total	Sulfur	Nitrogen
	Wt %				Wt%	ppm	
Project 114010							
PR-1251 (1:1 RCO/LCO Feed)	30,96	-	-	0,10	31,06	12700	3300
TLP PRODUCTS							
1st Pass Hydrotreating	13.0 - 21.7	8.3 - 18.2	0.1 - 0.2	0,00	21.4 - 40.1	888 - 1700	921 - 1400
2nd Pass Hydrotreating	5.6 - 11.9	16.5 - 22.0	1.5 - 5.2	0.4 - 1.4	24.0 - 40.5	10.4 - 24.7	98.1 - 249.1
1st Pass Hydrogenation	0.7 - 2.4	2.8 - 21.4	6.5 - 22.0	2.1 - 6.7	12.1 - 52.5	5.7 - 18.7	1.0 - 5.5
2nd Pass Hydrogenation	0.6 - 0.8	4.9 - 15.2	12.1 - 20.0	3.9 - 5.0	21.5 - 41.0	6.7 - 9.7	0.5 - 17.5
Project 114013							
FEED (550°F- Material) (1)	0.9 - 1.2	4.2 - 21.3	11.6 - 21.4	3.6 - 5.4	20.3 - 49.3	1.3 - 4.6	1.3 - 2.4
Hydrogenation	0.8 - 1.2	0.3 - 0.9	22.5 - 27.5	3.5 - 7.4	27.1 - 37.0	0.8 - 3.7	0.1 - 1.0
SR-0225 (2)	1,2	0,4	29,3	6,0	36,9	0,7	0,7
FEED (SR-0224) (3)	10,8	32,2	2,5	0,9	46,4	17,2	198,4
1st Pass Hydrogenation	0.5 - 0.8	16.4 - 27.0	14.0 - 22.7	4.0 - 5.3	34.9 - 55.8	1.8 - 4.1	23.1 - 78.8
2nd Pass Hydrogenation	1.1 - 1.2	0.2 - 1.0	36.4 - 39.6	5.4 - 6.8	43.1 - 48.6	0.8 - 1.4	0.3 - 2.0
SR-0226 (4)	1,2	0,5	38,3	6,0	46,0	0,9	0,8
SR-0227 (5)	1,2	0,4	33,0	6,0	40,6	0,5	0,1
SR-0227CT (6)	1,2	0,4	33,1	6,0	40,7	0,9	0,5

(1) Project 114010 hydrogenated TLP prod. distilled to remove the 550°F+ material from the feed for Project 114013

(2) The composition of the hydrogenated product from the distilled feed

(3) The composition of 1st pass hydrotreated jet fuel fraction product from previous PSU projects

(4) The composition of the 2nd pass hydrogenated product from the SR-0224 feed

(5) The blend of SR-0225 and SR-0226 products

(6) SR-0227 clay treated

Table 1-10

FINAL PRODUCT YIELDS AND ANALYSIS				
	Jet Fuel	Gasoline	Diesel	Fuel Oil
PARC Sample Code	SR-0225	SR-0230	SR-0228	SR-0229
Comments	(1)	(2)	(3)	(4)
PSU Sample Code	EI-171			
Product weight, lbs	2428	181,7	287,5	158,2
Yield, wt %	79,5	5,9	9,4	5,2
Sim Dist wt%(5890)				
IBP, °F	296	108	499	597
5, °F	343	187	529	622
10, °F	359	189	539	631
50, °F	401	269	577	682
95, °F	520	357	626	880
EP, °F	574	366	653	956
Specific Gravity, g/cc	0,8713	0,7976	0,9652	1,004
Sulfur, ppm	0,71	15,3	182,7	336,3
Nitrogen, ppm	0,70	5,3	13,4	381,3
Composition wt%				
Cyclohexane	0,50	6,24		
Xylenes	0,07	1,04		
Indan	0,24	0,25		
Indene	0,48	0,11		
t-decalin	29,33	4,16		
c-decalin	5,97	0,11		
Tetralin	0,41	-		
Naphthalene	1,21	-		
2-Methylnaphthalene	0,36	-		
1-Methylnaphthalene	1,05	-		
Ethylnaphthalenes	0,59	-		
Dimethylnaphthalenes	0,83	-		
Trimethylnaphthalenes	0,79	-		
T,P&H methyl-n's	0,64	-		
Other, 100 - All Naphthalenes	94,5	-		

- (1) SR-0225 is the jet fuel fraction from the 1st hydrogenation run of project 114013
(2) SR-0230 is the gasoline fraction from the 1st hydrogenation run of project 114013
(3) SR-0228 is the diesel fraction from the 1st hydrogenation run of project 114013
(4) SR-0229 is the fuel oil fraction from the 1st hydrogenation run of project 114013

Table 1-11

JET FUEL SUMMARY TABLE									
	<-US Mil Spec->		Commercial Samples			Project 114013			
PARC Sample Code			PR1630	PR1631		SR-0225	SR-0226	SR-0227	SR-0227
						(1)	(2)	(3)	Clay Treat
PSU Sample Code						EI-171	EI-172	EI-173	
Sim Dist wt%(5890)	JP-5	JP-8	JP-5	JP-5	JP-8				
IBP, °F			268	274	234	296	278	273	274
5, °F			309	320	301	343	343	338	338
10, °F	365 max	367 max	326	339	320	359	367	365	365
50, °F			398	413	397	401	387	389	389
95, °F			488	490	503	520	502	515	515
EP, °F	608 max	626 max	528	518	547	574	575	574	568
Specific Gravity, g/cc	.788-.845	.775-.840	0,8031	0,809		0,8713	0,8681	0,8702	0,8702
Sulfur, ppm	4000 max	3000 max	1300	1100		0,71	0,86	0,46	0,89
Nitrogen, ppm			0,494	9,58		0,70	0,76	0,09	0,46
Aromatics vol% (D1319)	25 max	25 max				1,3	1,5	1,6	2,0
Olefins vol% (D1319)	5 max	5 max				0,5	0,8	0,7	0,7
Saturates vol% (D1319)						98,2	97,6	97,7	97,3
Smoke Pt-PARC, mm (D1322)						25,5	26,0	22,8	24,9
Smoke Pt-PSU, mm (D1322)	19 min	19 min	24,57	23,95					
Carbon Deposit mg/cm2						36,93		7,62	1,63
Flash Point CC, °F (D93)	140 min	100 min	109,5	122,2		141,0	118,0	136,4	137,4
Flash Point OC, °F (D92)									
Composition wt%									
Cyclohexane			0,39	0,4		0,50	0,47	0,67	0,49
Xylenes			0,23	0,51		0,07	0,08	0,05	0,07
Indan			0,18	0,16		0,24	0,14	0,21	0,19
Indene			0,52	0,41		0,48	0,30	0,40	0,39
t-decalin			0,45	0,46		29,33	38,34	33,05	33,07
c-decalin			0,15	0,16		5,97	6,01	5,98	5,96
Tetralin			0,95	0,86		0,41	0,48	0,45	0,44
Naphthalene			0,51	0,71		1,21	1,17	1,20	1,19
2-Methylnaphthalene			0,58	0,79		0,36	0,17	0,27	0,27
1-Methylnaphthalene			0,37	0,42		1,05	1,35	1,19	1,19
Ethyl naphthalenes			0,63	0,68		0,59	0,56	0,58	0,59
Dimethylnaphthalenes			1,69	1,74		0,83	0,54	0,78	0,76
Trimethylnaphthalenes			0,04	-		0,79	0,20	0,47	0,59
T,P&H methyl-n's			0,4	1,89		0,64	0,20	0,56	0,50
Other, 100 - All Naphthalenes			95,8	93,8		94,5	95,8	95,0	94,9

(1) SR-0225 is the hydrogenated product from the blend of 150 still runs X-1103, 1104 & 1106 distilled to give 356°F to 518°F product

(2) SR-0226 is the product from the blend of past programs products previously distilled to give 356°F to 518°F material

(3) SR-0227 is the blend of both SR-0225 and SR-0226

Subtask 1.4 Fractionation into Refinery Product Slate

The total liquid product produced in Task 1.3 was distilled to provide fractions corresponding to gasoline, diesel, and fuel oil range refinery product streams as shown in **Table 1-10**. These materials will be used in many of the remaining tasks of the proposal. Distillation of the composite total liquid product is directed at evaluation of all non-jet fuel range material. Standard D2887 simulated distillation analysis were performed on gasoline, diesel and fuel oil fractions to insure that the boiling range of the fractions correspond to conventional refinery stream specifications. These materials were transferred to Penn State University for further evaluation.

Non-jet fuel range material produced and delivered to Penn State University for evaluation in this program includes:

EI-174	184.8 lbs gasoline
EI-175	399 lbs diesel
EI-176	167.6 lbs fuel oil

These materials are currently being characterized and results will be reported in future reports on this project.

Co-Coking Approach - Decant Oil Hydrotreating

Decant oil (Heavy FCC Cycle Oil) was hydrotreated at several different levels of severity to produce feeds for Penn State's co-coking component of the Refinery Integration Study. The Decant Oil was provided by United Refining, Warren

Pennsylvania and contained a high level of sulfur (3.5 wt%) and is a heavy oil with a high gravity (1.1203 gm/ml, API -5.2)

PARC's adiabatic hydrotreatment pilot unit, P67 was used for the hydrotreating.

The catalysts charges were:

Reactor 1 2148 ml, 2474 gm, Criterion NiMo Syncat-37

Reactor 2 2656 ml, 3060 gm, Criterion NiMo Syncat-37

Total 4804 ml, 5534 gm

Seven hydrotreated products were produced with a range of sulfur removal from 37.9 to 99.0 wt%.

Pilot Unit Description

In the configuration used for this study, P67 consists of two reactors operated in series. Three standard quench zones were included in the set up of Reactor 1 which contained catalytically inert quartz glass beads. Reactor 2 is not equipped with quench but heat loss does occur in the transfer line between the two reactors.

Hydrogen was recycled after amine scrubbing to remove H₂S and the purity was maintained at 95 to 98%. Minimum bleed off was used within the constraint of maintaining recycle H₂ purity. Make-up hydrogen is thereby minimized to supplying the

hydrogen consumed in the operation plus losses due to the on-line gas chromatograph demand.

The total liquid product was taken as fractionator bottoms after partial stripping of H₂S and ammonia in the fractionation tower. In some cases this operation resulted in small amounts of fractionation tower overhead. In such cases the furnace oil tower overhead was combined with the fractionation tower bottoms. The tower system was operated at atmospheric pressure.

Hydrotreating Operation

A sulfiding procedure was provided by the catalyst vendor and was modified to fit PARC's unit. The SYNCAT-37 catalyst was received pre-impregnated with a sulfur compound. A commercial diesel containing 0.25wt% sulfur as dimethyl disulfide in addition too the naturally occurring sulfur in the base diesel (about 300 ppm) was used as the catalyst activation feedstock. The sulfur in the feedstock would ensure that the catalyst had an adequate supply of sulfur during the sulfiding procedure. Catalyst bed temperatures were brought up to Rx 1 530°F and Rx 2 545°F prior to switching to run feed.

Operation on Run Feed -Run P67-69-1 Through 7

The run feed was set at 5500gm/hr. (about 1 LHSV) and the inlet hydrogen rate at 75 scf/hr. (2,400 scf/bbl). Inlet gas purity was initially targeted at 98 % hydrogen

minimum. Unit pressure was maintained at 600 psig for runs 1 through 5 and was increased to 1200 psig for runs 6 and 7.

The decant oil was processed for 10 days. Feed was processed at nominally seven different conditions representing seven levels of severity. To achieve this reactor temperature and feed rate were varied in the first four runs. The results for the first four runs confirmed our expectation that the decant oil difficult to desulfurize. Since the first drum of product (Run 1) had not achieved the target level of desulfurization it was decided to re-pass it at a reduced feed rate. The desulfurization level achieved was still only 82%. It was therefore decided, in the interest of time, to increase the reactor pressure to 1200 psig rather than reduce the feed rate further to achieve a target of about 95% desulfurization. Runs 5 and 6 achieved desulfurization levels of 88 and 99%, respectively. A decrease in reactor temperature was made in Run 7 to attempt to produce a product with a lower desulfurization level than the 88% of Run 5. However, the product maintained 99 % desulfurization in the limited time remaining.

A summary of the daily operating conditions for each run is given in **Table 1-12** together with the sulfur and nitrogen levels in the feed and the product. This information is further condensed in **Table 1-13** with the addition of the net weights and volumes of the seven samples shipped to Penn State. The API and specific gravities of the seven products are given in **Table 1-14**.

CATALYST		CRITERION SYNCAT-37 (PC-723)																						
CHARGE		ml	gm	Heats On 1100 2/3																				
Rx1		2148	2474	Start Diesel in 1100 2/4																				
Rx2		2656	3060	Start Run Feed: 2400 2/4 PR1542																				
Total		4804	5534	Pressure Test 1500 psig																				
		Runs 1-5 NOMINAL RUN PRESSURE 600 PSIG																Runs 6-7 NOMINAL RUN PRESSURE 1200 PSIG						
Run No	Time	Date	FEED gm/hr 8hrAv	REACTOR 1				REACTOR 2				WABT COMB 8HR AVG	LHSV 8HR AVG	Inlet gas SCFB	Quench SCFB	Makeup SCFB	%H2 INLET	HYDROGEN CONSUMP SCFB	WT. BAL % (8 HR)	PRODUCT ANALYSES				
				IN	OUT	MAX	WABT 8HR AVG	IN	OUT	MAX	WABT 8HR AVG									S, wt% (1)	N, PPM (1)	Spec Grav gm/ml	%DES	%DEN
	0000	2/5	Started Run Feed																	Feed Drum 1				
																			Feed Drum 3	3.44	1374	1.1203	-5.2 API	
																			Feed Drum 4					
P67-69-1	1430 grab	2/5	5490	529	594	594	556	545	615	615	581	568	1.02	2440	0	2611	98.2	975	100.9		1300	1.0760	100.0	0.0
	0800 grab	2/6	5490	530	596	596	557	545	614	614	582	570	1.02	2511	0	1786	98.2	685	99.0		1200	1.0760	100.0	7.7
P67-69-1	08-20	2/5-6	Product Drum No 1																	2.20	1300		37.9	0.0
P67-69-2	1600	2/6	Increasing temp																					
	04 grab	2/7	5274	560	666	666	603	577	637	637	610	606	0.98	2598	0	2148	97.7	908	99.0	1.67	1100	1.0679	52.8	
P67-69-2	20-08	2/6-7	Product Drum No 2																	1.75	1200		50.6	7.7
P67-69-3	0400	2/8	3875	567	687	687	622	590	651	651	629	626	0.72	3517	0	3428	97.9	1159	99.7	nr	nr	1.0575		
	04 grab	2/9	4144	568	685	685	621	590	647	647	626	624	0.77	3388	0	4879	98.7	1081	99.2	1.16	968	1.0568	67.2	
P67-69-3	08-04	2/7-9	Product Drum No 3																	1.22	1000		65.5	23.1
P67-69-4	0400	2/9	STARTED RAISING TEMPERATURES																				100.0	100.0
	15 grab	2/9	4090	607	716	716	668	632	678	678	663	666	0.76	3500	0	5577	97.5	1185	99.3	0.58	917	1.0568	83.6	
	08 grab	2/10	3821	608	712	712	669	662	692	692	680	675	0.71	3283	0	2626	95.7	1080	100	0.56	935	1.0583	84.2	
P67-69-4	04-16	2/9-10	Product Drum No 4																	0.64	944		81.9	27.4
P67-69-5	1600	2/10	STARTED 2ND PASS OF Drum No 1																					
	08 grab	2/11	2691	607	652	652	634	660	675	675	667	650	0.50	4602	0	1455	95.6	657	99.7	0.49	625	1.0451	86.2	
	900	2/11	STARTED RAISING TEMPERATURES																					
P67-69-5	16-12	2/10-11	Product Drum No 5																	0.42	678		88.1	47.8
P67-69-6	1345	2/11	STARTED RAISING PRESSURE TO 1200 PSIG																					
	08 grab	2/12	2745	686	786	786	753	716	757	757	744	749	0.51	4020	0	4775	95.2	1268	97.5	0.0087	78	1.0246	99.8	
	08 grab	2/13	2745	688	794	794	754	722	759	759	746	750	0.51	2858	0	4333	95.2	1288	97.1	0.0130	132	1.0239	99.6	
	12-08	2/11-13	Product Drum No 6																	0.0411	179	1.0254	98.8	86.2
																				0.0591	185			
	09	2/13	STARTED TO REDUCE TEMPARTURE																					
	1600	2/13	2745	655	771	771	735	694	740	740	733	734	0.51	3095	0	4587	97.2	1300	96.5					
	08-12	2/13																		0.0141	137		99.6	
	12-16	2/13																		0.0254	141		99.3	
	16-18	2/13																		0.0368	108		99.0	
	08-1800	2/13	Product Cans for Drum No 7																	0.0348	147	1.0224	99.0	88.7

Start Saving Product 0300, 2/5

(1) 2nd sample after re-mixing drum

Table 1-12. Hydrotreating Operating Conditions Summary

Catalyst CRITERION SYNCAT-37 (PC-723) Run Feed: UNITED REFINING DECANT OIL NOMINAL RUN PRESSURE 600 PSIG NOMINAL RUN PRESSURE 1200 PSIG																
Drum No	Run No	Time	Date 2004	Rx1	Rx2	Rx1+2	LHSV 8HR AV	Inlet gas Nominal SCFB	H2 Consup Nominal SCFB	PRODUCT ANALYSES					Net Wt. in drum	
				WABT 8HR AVG	WABT 8HR AVG	WABT 8HR AV				S, wt% (1)	N, PPM (1)	Spec Grav gm/ml	%HDS	%HDN	lbs	gallons
		0000	2/5	Started Run Feed						3.54	1300	1.1203	-5.2 API			
										3.44	1374					
1	P67-69-1	08-20	2/5-6	556	582	568	1.02	2500	750	2.20	1300	1.0810	37.9	0.0	26.4	2.9
2	P67-69-2	20-08	2/6-7	603	610	606	0.98	2600	908	1.75	1200	1.0730	50.6	7.7	133.8	15.0
3	P67-69-3	08-04	2/7-9	622	626	624	0.75	3450	1100	1.22	1000	1.0591	65.5	23.1	377.2	42.7
4	P67-69-4	04-16	2/9-10	669	680	675	0.74	3400	1150	0.64	944	1.0575	81.9	27.4	304.2	34.5
	P67-69-5	1600	2/10	STARTED 2ND PASS OF Drum No 1												
5	P67-69-5	16-12	2/10-11	634	667	650	0.50	4600	657	0.42	678	1.0489	88.1	47.8	91.6	10.5
	P67-69-6	1345	2/11	STARTED RAISING PRESSURE TO 1200 PSIG												
6	P67-69-6	12-08	2/11-13	754	745	750	0.51	3000	1268	0.0411	179	1.0254	98.8	86.2	260.8	30.5
										0.0591	185	(1)				0.0
7	P67-69-7	08-1800	2/13	735	733	734	0.51	3100	1300	0.0348	147	1.0224	99.0	88.7	49.9	5.9

(1) 2nd sample after re-mixing drum

Table 1-13. Product Drum Analyses

Table 1-14 Product Gravities and Weights

			weight, lbs		
	API	SpGr	Gross	Tare	Net
P67-69-1 (TLP Drum 1)	-0.6	1.0810	29.8	3.4	26.4
P67-69-2 (TLP Drum 2)	0.7	1.0703	149.6	15.8	133.8
P67-69-3 (TLP Drum 3)	2.1	1.0591	418.0	40.8	377.2
P67-69-4 (TLP Drum 4)	2.3	1.0575	345.0	40.8	304.2
P67-69-5 (TLP Drum 5)	3.4	1.0489	107.4	15.8	91.6
P67-69-6 (TLP Drum 6)	6.5	1.0254	301.6	40.8	260.8
P67-69-7 (TLP Drum 7)	6.9	1.0224	65.7	15.8	49.9

Delayed coking, used in petroleum refineries throughout the world, is a process that converts heavy petroleum residua (vacuum residua and decant oil) into light distillate fraction and coke. This is achieved by the pyrolysis and thermal degradation of the feedstock in a semi-continuous process, at temperatures between 450-500°C, in an inert atmosphere, and at pressures around 10 psig. The volatiles produced during the thermal degradation of the feedstock are vented during the operation, and transferred to a distillation tower, where they are fractionated into the appropriate distillates and the liquid products are recovered. These liquids can be further distilled to yield useful products for various industries. The coke product builds up in the reaction vessel over a period of 18 hours, at which point the feed is switched to pump into a parallel reaction vessel. The coke is then removed from the full vessel. The liquid products and coke produced have varying qualities that depend on feedstock and reaction conditions. A typical product distribution for a delayed coking operation is 70% liquids, 20% coke and 10 % gas.

Co-coking [1-25 – 1-27] involves the simultaneous co-carbonization of coal and petroleum resid in a delayed coking environment. A slurry of high volatile bituminous coal and decant oil is fed into a delayed coker drum at temperatures between 460 and 500 °C and at pressures between 10 and 150 psig. Under these conditions, the coal and decant oil become very fluid and coke to form a homogenous solid product.

The concept of co-coking stemmed from the need to produce coal-based liquids that would ultimately be converted into prototype thermally stable jet fuel, while relying on domestic fossil fuel resources. With the introduction of coal to the process stream it is assumed that the volatile constituents of coal may be produced along with the volatiles from the petroleum feed and subsequently fractionated.

Previous studies have determined that the compounds present in jet fuel that are derived from coal account for improved thermal stability. The following boiling point ranges for the liquid products of co-coking were used in this study: gasoline (Initial Boiling Point to 180 °C), jet fuel (180 °C-270 °C), diesel (270 °C -332 °C) and fuel oils (°332 °C-Final Boiling Point). It has been hypothesized that the yields of products in the given boiling range depends on the degree of hydrotreating of the decant oil feedstock. This report strives to determine a relationship between these two factors.

Materials

Analysis of the coal and decant oils used in this study was previously conducted by Escallon and Scalise [1-28].

Coal

Powellton/Eagle coal was procured from Markfork Cleaning Plant, Boone County, West Virginia. Two different versions were shipped from Preptech, Inc.

Fickinger [1-27] analyzed the properties of Eagle, which had similar properties to those of Powellton: location, proximate analysis, elemental analysis and temperature of maximum fluidity. Preptech Inc. had previously separated the Powellton/Eagle coal by particle size and density. The two slurry samples of about 15-20% solids contain:

- Cleaned coal coming from a column flotation cell. This sample has slightly lower ash yield.
- Cleaned coal coming from a conventional flotation cell. This sample has slightly higher ash yield.

The samples are an unknown blend of the Eagle and Powellton seams that have been separated by particle size and density during mechanical cleaning into a 100 X 0 (particles finer than 150 mm) particle size fraction that has been subjected to froth flotation either in a column or a bath.

Tables 1-15 and **1-16** give a summary of the proximate and ultimate analysis, fluidity, particle size distribution and ash mineral composition of the Powellton/Eagle coal.

Table 1-15. Proximate and Ultimate Analysis of Powellton/Eagle Coal (EI-106)

Proximate Analysis ^a	
Fixed Carbon %	64.61
Volatile Matter %	27.27
Ash %	8.12
Ultimate Analysis ^a	
Carbon %	80.92
Hydrogen %	4.55
Nitrogen %	1.28
Sulfur %	0.88
Oxygen % (by difference)	4.25
Fluidity Data ^b	
Fluid Temperature Range (°C)	88
Maximum Fluidity (ddpm)	7002
Softening Temperature (°C)	397
Particle Size Distribution ^c	
D[v,0.9]	Nd
D[v,0.5]	Nd
D[v,0.1]	Nd
Ash Mineral Composition ^d	
Silicon Dioxide	Nd
Aluminum Oxide	nd
Ferric Oxide	nd
Titanium Oxide	nd
Phosphorus Pentoxide	nd
Calcium Oxide	nd
Magnesium Oxide	nd
Sodium Oxide	nd
Potassium Oxide	nd
Sulfur Trioxide	nd

^a. Values reported on a dry basis

^b. Determined using a Geisler plastometer

^c. The D (v, 0.9), D (v, 0.5) and D (v, 0.1) values are the particle sizes where, respectively, 90,

50 and 10% of the particles, by volume, are less than the indicated size.

^d. Determined using ASTM D2795 and D3682

Table 1-16. Plasticity, Maceral content and Maximum Reflectance of Powellton/Eagle Coal

Analytical Procedure	Gieseler Plastometer		Organic Petrography, vol %			Ro
	T. at maximum fluidity (°C)	ddpm	Vitrinite	Liptinite	Inertinite	
Powellton/Eagle	446	7002	86.5	1.4	12.1	nd

Decant Oil

Decant oil was chosen based on the results found by Fickinger [1-27] and Martinez-Escandell [1-29]. Fickinger found a better interaction in decant oil/coal than for vacuum resid/coal while Martinez-Escandell observed higher anisotropy in aromatic feedstock (decant oil) than in the aliphatic feeds.

The decant oil was obtained from United Refining Corporation. This feed is used commercially for making premium needle coke. The ultimate analysis of the decant oil used in these experiments is shown in **Table 1-17**.

Table 1-17. Ultimate Analysis of the as Received Recant Oil (EI-107)

Ultimate Analysis ^a	
Carbon %	89.59
Hydrogen %	7.32
Nitrogen %	0.22
Sulfur %	2.99
Ash content (wt%) ^a	0.0
Conradson carbon residue Nd	
Asphaltene content	0.21

^a Values reported on a dry basis

The decant oil (EI-107) was hydrotreated at PARC Technical Services to provide a series of samples of decant oils with different levels of hydrotreating severity. These materials were characterized using a variety of analytical techniques. This information will be used to correlate decant oil structure and composition with the quality and yield of the product carbons produced by co-coking with coal.

The elemental analysis and H/C ratios for decant oil and hydrotreated decant oils are shown in **Table 1-18**. Hydrotreating severity increased with increasing EI-#. These results show that intermediate and severe hydrotreating was effective in reducing sulfur and nitrogen contents in the decant oil.

Table 1-18. Elemental Analysis of Hydrotreated Decant Oils

Sample ID	Carbon (As Det.)	Hydrogen (As Det.)	Nitrogen (As Det.)	Sulfur (As Det.)	Oxygen (As Det.)	H/C ratio
EI 107	89.59±0.27	7.32±0.13	0.22±0.08	2.99±0.01	-0.11	0.98
EI 133	90.09	8.40	0.18	1.39	-0.05	1.12
EI 134	89.93	8.98	0.24	0.94	-0.09	1.20
EI 135	90.80	8.71	0.17	0.44	-0.12	1.15
EI 136	90.23	8.98	0.50	0.33	-0.04	1.19
EI 137	90.02	10.00	0.10	0.03	-0.15	1.33
EI 138	90.59	9.24	0.12	0.02	0.03	1.22

FT-IR analysis of decant oils was used in characterization of these new feedstocks. **Figure 1-6** shows the IR of the original decant oil (EI-107) and its hydrotreated versions.

As the degree of hydrotreatment increases, the presence of free –OH groups decreases. The amount of aromatic material in the decant oil decreases, as expected, with increasing extent of hydrotreating. This can be seen by comparing the relative peak heights of aromatic C-H ($\sim 3030\text{ cm}^{-1}$) versus aliphatic C-H ($2960\text{--}2850\text{ cm}^{-1}$).

Figure 1-6. FT-IR of the Decant Oil and Hydrotreated Versions

Samples were analyzed on a Bruker AMX 360 NMR operating at 9.4 Tesla. Distillates were dissolved in CDCl_3 containing 0.1 vol % of tetramethylsilane (TMS) as a standard. A pulse delay of 45 seconds and a 70° tip angle were used to ensure quantitative results. Regions of the spectra were integrated and peaks were assigned based on literature chemical shift values for ^{13}C and ^1H [1-30]. (Tables 1-19 and 1-20).

Table 1-19. Proton N.M.R Assignments of Functional Groups in Carbonization Chemistry.

Band TMS (ppm)	Assignment
0.5-1.0	CH_3 g and further, some naphthenic CH and CH_2
1.0-1.7	CH_2 b and further, some b CH_3
1.7-1.9	Most CH, CH_2 b hydroaromatic
1.9-2.1	a to olefinic.
2.1-2.4	CH_3 a to aromatic carbons
2.4-3.5	CH, CH_2 a to aromatic carbons
3.5-4.5	CH_2 bridge (diphenylmethane)
4.5-6.0	Olefinic
6.0-7.2	Single ring aromatic
7.2-8.3	Diaromatic and most of tri- and tetraaromatic
8.3-8.9	Some tri- and tetraaromatic rings
8.9-9.3	Some tetraaromatic rings

Table 1-20. Carbon N.M.R Assignments of Functional Groups in Petroleum Carbonization Chemistry.

Band TMS (ppm)	Assignment
11.0-12.5	CH ₃ g and further from aromatic ring CH ₃ in ethyl substituted cyclohexane
12.5-15.0	CH ₃ g and further from aromatic ring CH ₃ a shielded by two adjacent rings or groups
15.0-18.0	CH ₃ a shielded by one adjacent ring or group Some CH ₃ a hydroaromatic and naphthenic CH ₂
18.0-20.5	CH ₃ a shielded by one adjacent rings or group Some CH ₃ a hydroaromatic and naphthenic CH ₂
20.5-22.5	CH ₃ not shielded by adjacent rings or groups Some CH ₃ a hydroaromatic and naphthenic CH ₂
22.5-24.0	CH ₂ g and further adjacent to terminal CH ₃ CH ₂ b in unsubstituted tetralin structures
24.0-27.5	Some CH ₂ naphthenic CH ₂ a not shielded CH ₂ b in propyl and indan groups CH ₃ b in isopropyl
27.5-37.0	CH ₂ not adjacent to CH in alkyl groups CH ₂ adjacent to alkyl CH in some CH ₂ a and CH ₂ adjacent to terminal CH ₃ in alkyl substituents with more than four carbons CH ₂ in ring joining ethylene groups Some CH ₂ naphthenic Some ring joining methylene (32-43 ppm)
37.0-60.0	CH alkyl groups (except isoalkyl) CH naphthenic CH ₂ alkyl groups adjacent to CH Some ring joining methylene (32-43 ppm)
108.0-118.0	Some olefinic (others spread through aromatic region)
118.0-129.5	Protonated aromatic Some internal (quaternary) aromatic
129.5-133.0	Most internal aromatic
133.0-135.0	Methyl substituted aromatic
135.0-138.0	Naphthenic substituted aromatic
138.0-160.0	Alkyl (other than methyl) substituted aromatic Heteroatom (N, O, S) aromatic

The samples of decant oil and hydrotreated versions were diluted in deuterated chloroform with 0.1 vol % of tetramethylsilane (TMS) for ¹H-NMR analysis. Band assignments for integrating intensities for the decant oil and hydrotreated versions were

selected by using the integrated intensities given by Rodriguez [1-30]. The results are listed in **Table 1-21**.

Table 1-21: Proton NMR Analysis of Functional Groups for the Decant Oils

Band TMS (ppm)	EI-107	EI-133	EI-134	EI-135	EI-136	EI-137	EI-138
	<i>%</i>						
0.5-1.0	5.0	5.4	6.1	6.3	5.8	5.6	5.5
1.0-1.7	11.1	12.3	12.3	12.4	12.4	12.3	12.3
1.7-1.9	0.8	1.0	1.5	1.1	1.0	1.2	1.0
1.9-2.1	1.0	1.0	1.6	1.4	1.1	1.1	1.1
2.1-3.5	37.4	40.2	38.4	38.5	39.5	39.4	39.9
3.5-4.5	1.6	2.3	2.0	1.8	2.1	2.1	2.3
4.5-6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.0-7.2	5.0	4.7	4.7	4.2	4.2	3.3	3.9
7.2-8.3	32.7	27.8	27.2	28.0	28.1	28.4	28.3
8.3-8.9	5.0	5.0	5.4	5.6	5.3	5.9	5.4
8.9-9.3	0.3	0.3	0.9	0.7	0.5	0.6	0.4
Poly-Ar*	38.0	33.1	33.5	34.2	33.9	34.9	34.2
Mono/poly - Ar	7.5	7.0	7.2	8.1	8.1	10.5	8.9

Polyaromatics have been defined as aromatics containing two or more rings. In future work, the decant oil and hydrotreated versions will be analyzed by ^{13}C NMR.

API gravities were calculated from densities for each of the decant oils in this series. These are shown in **Table 1-22**.

Table 1-22. Densities and API Gravity of Decant Oils

Sample ID	Density (g/mL)	API	T (F)	API	API corrected at 60°F
EI-107	1.11	4.44	81.5	-4.4	---
EI-133	1.07	1.07	79.9	1.1	0.3
EI-134	1.06	2.25	80.6	2.2	1.4
EI-135	1.06	2.59	80.6	2.6	1.8
EI-136	1.05	3.66	81.5	3.7	2.8
EI-137	1.02	6.96	82.4	7.0	6.1
EI-138	1.02	7.26	80.6	7.3	6.4

The temperature correction at 60°F was carried out by using Table 5A according to the ASTM standard D-1250. The table is reported in “Petroleum Measurement Tables” [1-31].

The asphaltene content of the decant oil and hydrotreated versions was determined using the procedure defined in ASTM D1250-80 [1-32]. Asphaltene content was determined three times for each decant oil and averaged. The results are summarized in **Table 1-23**.

Table 1-23. Asphaltene Content of Decant Oils

	EI-107	EI-133	EI-134	EI-135	EI-136	EI-137	EI-138
1	0.22	0.08	0.07	0.16	0.15	0.24	0.26
2	0.23	0.07	0.08	0.16	0.16	0.22	0.25
3	0.17	0.05	0.08	0.13	0.17	0.23	0.27
Mean	0.21	0.07	0.08	0.15	0.16	0.23	0.26
Standard deviation	0.03	0.02	0.01	0.02	0.01	0.01	0.01

Average boiling points (°C) were measured from simulated distillation data for each of the hydrotreated decant oils as well as the parent material. These are summarized in **Table 1-24**.

Table 1-24. Average Boiling Points of Decant Oil and Hydrotreated Decant Oils

Sample ID	Average Boiling Point °C
EI-107	414.6
EI-133	400.7
EI-134	392.9
EI-135	391.4
EI-136	388.0
EI-137	370.1
EI-138	371.0

III. Equipment and Procedures

Co-coking studies were carried out in a pilot-scale delayed coker (PSDC).

Pilot – Scale Delayed Coker (PSDC)

A pilot-scale delayed coker at The Energy Institute at The Pennsylvania State University was modified to provide reliable continuous delayed coking for 4-6 hours to provide acceptable quantities of cokes for evaluation. The coke drum has internal dimensions of 7.5 cm ID by 102.5 cm high, giving a volume of 4.5 liters. The unit is capable of operating under most delayed coking process conditions. The system pressure, temperature and flow rates are monitored by a number of computer-controlled devices, and data from these devices is recorded throughout the run.

The preheater was modified to provide reliable continuous operation for 4-6 hours without pressure buildup due to plugging. The 3/8 inch coiled preheater was replaced by a one-inch diameter, 20” straight preheater. By increasing the diameter of the preheater, and eliminating the tight radius of curvature for a coiled preheater required by the oven

dimensions, the unit has been made more dependable. The pilot-scale coking unit was further improved by including thermocouples at both the inlet and exit of the preheater. This provides the capability to monitor the temperature gradient through the preheater and to know the temperature of feed entering the coke drum. The following operating conditions were set for the coking experiments: coke drum inlet temperature 465 °C, coke drum pressure 25 psig, decant oil feed rate 16.7 g/min, and length of run 360 minutes. At the conclusion of the run the mass of the liquid condensate was measured. In addition, the height of the coke bed was measured prior to removing the coke as a plug and weighing the materials.

The pilot-scale laboratory coker unit used in these experiments is shown in **Figure 1-7**.

Figure 1-7. Laboratory Coker Unit

The products from these co-coking experiments provide sufficient material to give products for further evaluation (**Figure 1-8**). Shown are the gasoline, jet fuel, diesel, fuel oil and coke from coking decant oil and co-coking decant oil and 20% coal.

Figure 1-8. Products of Coking and Co-Coking

Co-coking feedstock

The liquid products from seven co-coking studies were analyzed to determine the proportion of materials in each of the refinery cut boiling ranges: gasoline, diesel and fuel oil.

The feedstock of the first control experiment, Run 26, contained only decant oil (sample EI-133). The six subsequent co-coking experiments (Runs 27-32) used feedstocks in an 80:20 ratio of decant oil or hydrotreated decant oil to coal; and the severity of hydrotreatment increased with increasing run number. The decant oils used were EI-133 to EI-138, as analyzed in the previous section, with EI-138 having the

greatest degree of hydrotreating. Conditions and product yields from each of the co-coking runs are summarized in **Table 1-25**.

Table 1-25. Co-Coking Conditions and Product Yields (Runs 26-32)

Run #	26	27	28	29	30	31	32
Conditions	DO	DO/Coal	DO/Coal	DO/Coal	DO/Coal	DO/Coal	DO/Coal
		80/20	80/20	80/20	80/20	80/20	80/20
	DO= EI-133	DO= EI-133	DO= EI-134	DO= EI-135	DO= EI-136	DO= EI-137	DO= EI-138
		C= EI-106	C= EI-106	C= EI-106	C= EI-106	C= EI-106	C= EI-106
feedstock, hours	6	6	6	6	6	6	6
hold at 500C, hrs	6	6	6	6	6	6	6
feed rate, g/min	16.7	16.7	16.7	16.7	16.7	16.7	16.7
preheater inlet, C	228	230	236	227	223	225	224
preheater outlet, C	441	456	440	443	445	439	425
coke drum inlet, C	475	470	470	460	462	468	472
coke drum lower/middle, C	472	472	471	470	470	473	468
coke drum top, C	480	474	472	474	473	478	472
Material Fed to Reactor	5900	6093	5948	5752	6229	6076	5926
Products							
Coke	45	1099	1453	1079	990	1130	1068
Liquid	5454	4366	4220	4157	4727	4532	4513
Gas (by difference)							
preheater contents	136	142	147	133	143	131	113
coke +liquid product	5499	5465	5673	5236	5717	5662	5581
liquid/coke	121.20	3.97	2.90	3.85	4.77	4.01	4.23
%coke	0.76%	18.04%	24.43%	18.76%	15.89%	18.60%	18.02%
%liquid product	92.44%	71.66%	70.95%	72.27%	75.89%	74.59%	76.16%
%gas							

The boiling point distribution of the liquid products was determined using vacuum distillation and simulated distillation. Vacuum distillation was carried out using approximately 1200 g of the liquid products from the co-coking run. The liquid product from each co-coking experiment was separated by boiling point into four fractions and then analyzed. The first fraction, denoted the gasoline fraction, contained the portion of the product with boiling points less than 180°C. The subsequent fractions were the jet fuel fraction, diesel fraction and fuel oil fraction with boiling point distributions between 180°C and 270°C, between 270°C and 332°C, and above 332°C, respectively.

Simulated Distillation

The accuracy of each vacuum distillation was analyzed using Simulated Distillation according to ASTM 2887. The gas chromatograph that was used was an HP Series II, 5890 Gas Chromatograph. The gasoline, jet fuel and diesel samples recovered from the vacuum distillation were each analyzed to determine the boiling point distribution of the fractions. Boiling point data was recorded by weight percentage and was then used to correct the yield percentages from the vacuum distillation.

Vacuum Distillation

The yields of gasoline, jet fuel, diesel, and fuel oils from the liquid products of the co-coking studies as determined by vacuum distillation are summarized in **Tables 1-26 and 1-27**.

Table 1-26. Liquid Product Boiling Point Distribution by Weight and Percent Recovery

Recovered Fractions Weight (g)	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
Sample Weight (g)	1278	1202	1205	1227	1268	1251	1217
gasoline	9	32	27	25	19	23	26
jet fuel	42	40	55	62	71	93	123
diesel	216	123	157	206	288	328	288
fuel oil	1000	991	960	925	885	802	749
Percent Recovery (%Wt)	99.14	98.67	99.50	99.27	99.61	99.60	97.45

Table 1-27. Liquid Product Boiling Point Distribution by Weight Percentage

Product Yields, %Weight	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
gasoline	0.70	2.66	2.24	2.04	1.50	1.84	2.14
jet fuel	3.29	3.33	4.56	5.05	5.60	7.43	10.11
diesel	16.90	10.23	13.03	16.79	22.71	26.20	23.66
fuel oil	78.25	82.45	79.67	75.39	69.79	64.10	61.54

This preliminary data suggests that the hydrotreatment causes an increased yield of jet fuel. The yield of jet fuel ranges from 3.29 to 10.11% of the total liquid products for Runs 26 through 32, respectively.

Simulated Distillation

Simulated distillation was used to test the accuracy of the vacuum distillation results. The resulting boiling point distributions of each of the three fractions, gasoline, jet fuel, and diesel, are listed in **Table 1-28**.

Table 1-28. Simulated Distillation Boiling Point Distribution Data by Weight Percentage

°C	Run 26			Run 27			Run 28		
	Gasoline	Jet Fuel	Diesel	Gasoline	Jet Fuel	Diesel	Gasoline	Jet Fuel	Diesel
IBP-180	92.01	2.21	-	91.34	8.48	-	76.76	1.36	-
180-270	7.99	91.82	10.63	8.66	89.79	26.34	23.24	89.72	17.91
270-332	-	5.97	53.06	-	1.73	69.03	-	8.92	75.08
332-FBP	-	-	36.31	-	-	4.63	-	-	7.01
°C	Run 29			Run 30					
	Gasoline	Jet Fuel	Diesel	Gasoline	Jet Fuel	Diesel			
IBP-180	85.40	5.01	-	91.63	5.72	-			
180-270	14.60	89.00	17.22	8.37	86.51	26.28			
270-332	-	5.99	74.81	-	7.77	72.43			
332-FBP	-	-	7.97	-	-	1.30			
°C	Run 31			Run 32					
	Gasoline	Jet Fuel	Diesel	Gasoline	Jet Fuel	Diesel			
IBP-180	93.76	6.80	-	89.25	3.32	-			
180-270	6.24	90.73	31.66	10.75	86.69	18.47			
270-332	-	2.47	65.76	-	9.98	77.42			
332-FBP	-	-	2.58	-	-	4.11			

These results show that the gasoline fractions, in general, contain approximately 11-35% material that boils in the jet fuel range, 180-270 °C. Jet fuel fractions begin close to 180 °C; however, these fractions also contain significant amounts of the diesel range material, 270-332°C. Jet fuel from Runs 29 and 32 were especially contaminated with material that boiled over 270°C, 41.68% and 33.8% material, respectively. The diesel range was also found to contain 10-25% of liquids boiling in the jet fuel range. To account for these errors, these values were then used to correct the percentage yields from vacuum distillation. These results are listed in **Tables 1-29 and 1-30**.

Table 1-29. Corrected Weights of Product Fractions Isolated from Vacuum Distillation

Recovered Weight (g)	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
Gasoline	9	33	21	24	21	28	27
jet fuel	62	71	84	94	139	190	163
Diesel	117	86	123	158	214	218	235
fuel oil	1078	997	971	941	889	810	761

Table 1-30. Corrected Liquid Product Boiling Point Distribution (Weight Percentage)

Product Yields, %Weight	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
gasoline	0.72	2.71	1.78	1.99	1.69	2.23	2.24
jet fuel	4.87	5.91	6.95	7.69	10.94	15.16	13.36
diesel	9.16	7.12	10.19	12.86	16.89	17.43	19.33
fuel oil	84.38	82.92	80.58	76.73	70.09	64.79	62.52

These yields were then related to the total liquid product yields from the co-coking run to give the actual yield of gasoline, jet fuel, diesel and fuel oil for each co-coking run. The actual weight percent yields are listed in **Table 1-31**.

Table 1-31. Co-Coking Percent Yields: Liquid Products

Product Yields, %Weight	Run 26	Run 27	Run 28	Run 29	Run 30	Run 31	Run 32
total liquid products	92.44	71.66	70.95	72.27	75.89	74.59	76.16
gasoline	0.52	2.51	1.26	1.44	1.29	1.66	1.71
jet fuel	4.50	5.47	4.93	5.55	8.30	11.31	10.18
diesel	8.47	6.58	7.23	9.30	12.81	13.00	14.72
fuel oil	78.00	76.65	57.17	55.45	53.19	48.32	47.61

The results from vacuum distillation and simulated distillation reveal that the percentage of the liquid products corresponding to jet fuel increases with increasing hydrotreatment. The percentage of liquid products boiling in the jet fuel range, 180-270 °C, ranges from 4.5-11.3%, with the higher end corresponding to a more hydrotreated decant oil. The amount of jet fuel, however, decreases slightly from Run 31 (11.31%) to

Run 32 (10.18%). Similarly, the overall yield of jet fuel in the co-coking run increases with higher degree of hydrotreating. Additionally, the total liquid product yield decreases with the addition of coal to the decant oil. The total liquid is 92.44% for Run 26, which contained only decant oil feedstock, compared to approximately 70-75% for the runs containing decant oil or hydrotreated decant oil.

It is also worth noting that the yields of gasoline, jet fuel and diesel increase with increasing hydrotreatment; however, the yield of fuel oil decreases with increasing hydrotreatment. The total percentage that corresponds to gasoline is approximately 0.5-2.5% and that of diesel is 6.5-15% for low to high degrees of hydrotreatment, respectively; whereas the total percentage corresponding to fuel oil ranges from approximately 78-48% for low to high degrees of hydrotreatment, respectively.

While this information provides a good basis for determining the relationship between severity of hydrotreating and product yield, further analysis is needed to determine the best co-coking conditions to produce thermally stable jet fuel. For example, the jet fuel fractions will need to be analyzed to determine their chemical composition and the need to further hydrotreat the jet fuel fraction to provide optimal thermal stability.

The combined liquid samples were characterized using simulated distillation and ^1H and ^{13}C NMR analysis. Samples were analyzed using a Bruker AMX 360 NMR operating at 9.4 Tesla. Samples were dissolved at a 1/1 volume ratio in CDCl_3 containing 1 vol % of tetramethylsilane (TMS) as standard. A pulse width of 5 μsec , pulse delay of 5 sec for ^1H

and of 45 seconds for ^{13}C and 90° tip angle were used to ensure quantitative results. For the ^{13}C analyses, 20 mg $\text{Cr}(\text{AcAc})_3$ was used for 2 mL of overhead liquid/ CDCl_3 mixture. Regions of the spectra were integrated and peaks were assigned based on literature chemical shift values for ^1H and ^{13}C .³⁰

The ^1H and ^{13}C nmr results are summarized in Tables 1-32 and 1-33. These data show that liquid distillate product from each of the reactions using decant oil alone, co-coking the decant oil with coal and co-coking followed by steam strip contain essentially the same amounts of aliphatic hydrogen and carbon and aromatic hydrogen and carbon. This implies that the liquid composition is not greatly perturbed by the coal.

In a separate set of experiments liquid samples collected at 60, 180 and 360 minutes into the co-coking experiment were characterized using ^1H and ^{13}C NMR, **Tables 1-34 and 1-35**, respectively. The results show that there is little change in the composition as the reaction proceeds. This implies that the carbonaceous solid in the coke drum does not significantly influence the composition of the liquid distillate that is recovered as overhead.

Table 1-32. Distribution of ^1H NMR signal of combined oils from coking and co-coking experiment.

Assignment	Band (ppm)	DO only	DO/Coal	DO/Coal//SS
CH_3 γ and further, some naphthenic CH and CH_2	0.5-1.0	17.8	17.2	17.9
CH_2 β and further, some β CH_3	1.0-1.7	39.2	40.6	39.7
Most CH, CH_2 β hydroaromatic	1.7-1.9	1.9	2.1	2.0
α to olefinic	1.9-2.1	2.5	2.6	2.7
CH_3 α to aromatic carbons	2.1-2.4	8.1	7.8	7.9
CH, CH_2 α to aromatic carbons	2.4-3.5	9.2	9.7	9.6
CH_2 bridge (diphenylmethane)	3.5-4.5	0.2	0.3	0.1
Olefinic	4.5-6.0	0.4	0.4	0.4
	Aliphatic (total)	79.3	80.7	80.3
Single ring aromatic	6.0-7.2	5.3	5.2	4.8
Diaromatic and most of tri- and tetraaromatic	7.2-8.3	14.0	12.8	13.4
Some tri- and tetraaromatic rings	8.3-8.9	1.3	1.2	1.4
Some tetraaromatic rings	8.9-9.3	0.0	0.0	0.0
	Aromatic (total)	20.6	19.2	19.6

Table 1-33. Distribution of ^{13}C NMR signal of combined oils from coking and co-coking experiment.

Assignment	Band (ppm)	DO only	DO/Coal	DO/Coal//SS
$\text{CH}_3\gamma$ and further from aromatic ring	11.0-12.5	0.4	0.4	0.6
CH_3 in ethyl substituted cyclohexane				
$\text{CH}_3\gamma$ and further from aromatic ring	12.5-15.0	3.2	3.2	3.5
$\text{CH}_3\alpha$ shielded by two adjacent rings or groups				
$\text{CH}_3\alpha$ shielded by one adjacent ring or group	15.0-18.0	1.4	1.4	1.6
Some CH_3 a hydroaromatic and naphthenic CH_2				
$\text{CH}_3\alpha$ shielded by one adjacent rings or group	18.0-20.5	3.8	3.8	4.2
Some CH_3 a hydroaromatic and naphthenic CH_2				
CH_3 not shielded by adjacent rings or groups	20.5-22.5	3.8	3.7	4.0
Some CH_3 a hydroaromatic and naphthenic CH_2				
$\text{CH}_2\gamma$ and further adjacent to terminal CH_3	22.5-24.0	3.1	3.1	3.1
$\text{CH}_2\beta$ in unsubstituted tetralin structures				
Some CH_2 naphthenic, $\text{CH}_2\alpha$ not shielded	24.0-27.5	3.7	3.6	3.9
$\text{CH}_2\beta$ in propyl and indan groups, $\text{CH}_3\beta$ in isopropyl				
CH_2 not adjacent to CH in alkyl groups	27.5-37.0	22.6	23.6	22.8
CH_2 adjacent to alkyl CH in some CH_2 a and CH_2 adjacent to terminal CH_3 in alkyl substituents with more than four carbons				
CH_2 in ring joining ethylene groups, some CH_2 naphthenic				
Some ring joining methylene (32-43 ppm)				
CH alkyl groups (except isoalkyl), CH naphthenic	37.0-60.0	8.6	9.3	8.2
CH_2 alkyl groups adjacent to CH				
Some ring joining methylene (32-43 ppm)				
Some olefinic (others spread through aromatic region)	108.0-118.0	0.6	0.6	1.5
Protonated aromatic	118.0-129.5	30.9	28.8	30.5
Some internal (quaternary) aromatic				
Most internal aromatic	129.5-133.0	6.6	6.6	6.3
Methyl substituted aromatic	133.0-135.0	2.5	2.6	2.4
Naphthenic substituted aromatic	135.0-138.0	8.7	9.3	7.5
Alkyl (other than methyl) substituted aromatic Heteroatom (N, O, S) aromatic	138.0-160.0	0.4	0.4	0.6
Aromatics (total)		49.3	47.9	48.2

Table 1-34. Distribution of ^1H NMR signal of co-coking of Pittsburgh coal with decant oil

Assignment	Band (ppm)	60min.	180min.	360min.	Mean	Std. Dev.
CH_3 γ and further, some naphthenic CH and CH_2	0.5-1.0	6.2	6.0	6.7	6.27	0.36
CH_2 β and further, some β CH_3	1.0-1.7	15.4	13.5	13.0	13.95	1.29
Most CH, CH_2 β hydroaromatic	1.7-1.9	1.0	1.4	1.6	1.33	0.33
α to olefinic	1.9-2.1	3.3	5.0	6.2	4.82	1.45
CH_3 α to aromatic carbons	2.1-2.4	19.2	20.5	21.2	20.30	1.04
CH, CH_2 α to aromatic carbons	2.4-3.5	13.7	9.9	7.6	10.39	3.07
CH_2 bridge (diphenylmethane)	3.5-4.5	0.4	0.2	0.1	0.27	0.16
Olefinic	4.5-6.0	0.1	0.1	0.4	0.19	0.21
	Aliphatic (total)	59.3	56.6	56.9	57.52	1.49
Single ring aromatic	6.0-7.2	12.0	14.5	15.2	13.89	1.65
Diaromatic and most of tri- and tetraaromatic	7.2-8.3	26.5	27.4	26.6	26.85	0.50
Some tri- and tetraaromatic rings	8.3-8.9	1.5	0.9	0.7	1.06	0.38
Some tetraaromatic rings	8.9-9.3	0.7	0.6	0.6	0.67	0.06
	Aromatic (total)	40.7	43.4	43.1	42.48	1.49

Table 1-35. Distribution of ^{13}C NMR signal of co-coking of Pittsburgh coal with decant oil

Assignment	Band, (ppm)	60min.	180min.	360min.	Mean	Std Dev.
CH ₃ γ and further from aromatic ring	11.0-12.5	0.2	0.1	0.2	0.2	0.06
CH ₃ in ethyl substituted cyclohexane						
CH ₃ γ and further from aromatic ring	12.5-15.0	1.7	1.5	1.4	1.6	0.1
CH ₃ α shielded by two adjacent rings or groups						
CH ₃ α shielded by one adjacent ring or group	15.0-18.0	1.5	1.5	1.4	1.5	0.1
Some CH ₃ a hydroaromatic and naphthenic CH ₂						
CH ₃ α shielded by one adjacent rings or group	18.0-20.5	4.7	4.4	4.4	4.5	0.2
Some CH ₃ a hydroaromatic and naphthenic CH ₂						
CH ₃ not shielded by adjacent rings or groups	20.5-22.5	4.5	4.3	4.4	4.4	0.1
Some CH ₃ a hydroaromatic and naphthenic CH ₂						
CH ₂ γ and further adjacent to terminal CH ₃	22.5-24.0	1.1	0.8	0.9	0.9	0.1
CH ₂ β in unsubstituted tetralin structures						
Some CH ₂ naphthenic, CH ₂ α not shielded	24.0-27.5	1.1	1.0	1.1	1.0	0.1
CH ₂ β in propyl and indan groups, CH ₃ β in isopropyl						
CH ₂ not adjacent to CH in alkyl groups	27.5-37.0	7.4	6.5	6.8	6.9	0.4
CH ₂ adjacent to alkyl CH in some CH ₂ a and CH ₂ adjacent to terminal CH ₃ in alkyl substituents with more than four carbons						
CH ₂ in ring joining ethylene groups						
Some CH ₂ naphthenic, ring joining methylene (32-43 ppm)						
CH alkyl groups (except isoalkyl), CH naphthenic	37.0-60.0	2.3	2.1	2.7	2.4	0.3
CH ₂ alkyl groups adjacent to CH						
Some ring joining methylene (32-43 ppm)						
Some olefinic (others spread through aromatic region)	108.0-118.0	1.1	1.0	1.5	1.2	0.3
Protonated aromatic, some internal (quaternary) aromatic	118.0-129.5	47.7	48.9	50.2	48.9	1.3
Most internal aromatic	129.5-133.0	10.9	11.1	10.6	10.9	0.3
Methyl substituted aromatic	133.0-135.0	3.9	3.9	3.8	3.9	0.1
Naphthenic substituted aromatic	135.0-138.0	12.0	12.8	10.5	11.8	1.1
Alkyl (other than methyl) substituted aromatic Heteroatom (N, O, S) aromatic	138.0-160.0	0.2	0.1	0.2	0.2	0.06
	Aromatics	75.6	77.7	76.7	76.7	1.1
	(total)					

Task 2. Evaluation of Coal-based Gasoline and Diesel Products in IC Engines and Related Studies

By introducing coal-derived streams into the refinery, several perturbations to the quality and quantity of refinery streams may result and directly impact vehicular fuels production. The coal contribution to the refinery streams will affect the quality, composition and performance of the resulting vehicular fuels. The fraction of the hydrotreated streams that boils below 180°C will be directed to the gasoline pool. Having components from coal is expected to boost octane number and aromatic content, and therefore, boost value. The >270°C cut of the hydrotreated stream would be low in sulfur due to the severe hydrotreatment. The effect on flash point will need to be determined if this stream is sent to the fuel oil pool and/or diesel pool. If this stream is combined with diesel fuel, it will add cycloparaffins, which will increase energy density and boost value. However, the impact on cetane number and sooting tendency is unclear. The following task structure will permit assessment of the impact of refinery integration of JP-900 production on gasoline and diesel fuel.

Subtask 2.1. Impact on Gasoline Quality and Performance

Under this subtask, our efforts have consisted of continuing preparation and refinement of facilities for the SI engine testing activity and ignition studies of relevant compounds to understand the impact of the coal-derived compounds on knocking and flame propagation.

Subtask 2.1.1. Preparation of Laboratory and Instrumentation

Under this subtask, we acquired and installed the Ricardo Hydra single-cylinder research engine for use under Task 2.1.2 and developed instrumentation for combustion analysis. **Figure 2-1** shows the Ricardo Hydra single-cylinder research engine in the laboratory at the Energy Institute. We have configured a National Instruments “PXI” data acquisition system and Labview software to operate the engine and perform real-time combustion analyses. A screen capture for this Labview interface is shown below in **Figure 2-2**, which includes real-time heat release analysis and general data logging. **Figure 2-3** shows the modified fuel delivery system for the ignition quality tests.

Combustion and emission properties of the coal-based gasoline in SI engine application will be studied in a single-cylinder Ricardo Hydra research engine and a single-cylinder Waukesha CFR octane rating engine.

GC-MS result has shown that the major components in the coal-based gasoline samples are cycloalkanes, whose octane ratings are lower than that of the commercial-grade gasoline and therefore may cause knocking in SI engine combustion. Flame propagation across the combustion chamber and the auto-oxidation chemistry of the unburned mixture (end gas) have been identified as the two determining factors in engine knock.

A head gasket equipped with 6 ion probes (**Figure 2-4**) has been designed and fabricated for the Hydra engine which enables detecting the flame arrival along the plane of head gasket. The related signal conditioning board has been build and data acquisition boards have been purchased. Another in-cylinder flame detector, optical sensor equipped

spark plug, will be obtained soon which allows the flame detection on the top of the combustion chamber.

The auto-oxidation chemistry of the end gas is being performed at a Waukesha CFR octane rating with modified intake system and running at the motoring mode.

Figure 2-1 Ricardo “Hydra” Single-Cylinder Research Engine and Bedplate in the Diesel Combustion and Emissions Laboratory

Figure 2-2 Screen image of the Labview data acquisition interface for operating and performing data logging from the Ricardo Hydra engine

Figure 2-3 Fuel Delivery Apparatus to Provide Premixed Prevaporized Fuel Samples to the CFR Octane Rating Engine for Ignition Studies

Figure 2-4 Ion probe equipped head gasket for the Hydra engine

Subtask 2.1.2 Impact on Chemical and Physical Properties

Under this subtask, we have performed detailed chemical analyses and physical analyses of fuel samples. From several runs at PARC, fuel fractions were provided representing the gasoline and diesel fuel cuts. To date the primary fuel characterization for the gasoline cut has been through ignition studies that are presented under Subtask 2.1.3 below.

Subtask 2.1.3 Impact on SI Engine Emissions and Performance

Model compounds (cyclohexane and methylcyclohexane) for the coal-based gasoline have been studied in the modified CFR octane rating engine for their low temperature oxidation chemistry. The intake air at ambient pressure is heated to 260 C and the fuel is injected into the heated air at the pressure of 700 psi. Fuel vaporizes and is subsequently heated to 260 C before entering the engine. Engine runs at motoring mode (without spark ignition) at 900 rpm with the compression ratio increasing gradually to achieve auto-ignition. A Kistler pressure transducer records the cylinder pressure which is used to calculate the heat release and bulk temperature time history during one engine cycle via an in-house Labview program. Intake air is diluted by nitrogen at 100 SCFH in order to avoid violent engine knocking at ignition. FT-IR and GC-MS are respectively used to analyze the gaseous and condensed species in the engine exhaust. Equivalence ratio from 0.25 to 2.0 for both model compounds was studied.

Heat release calculation for the model compounds autoignition shows that there is no low temperature heat release occurring prior to the main combustion. A typical heat

release profile at autoignition for cyclohexane and methylcyclohexane is shown in **Figure 2-5**. Single-stage ignition was observed for cyclohexane throughout the equivalence ratio studied. Methylcyclohexane exhibits the same thing except that a quasi two-stage ignition appears at $\phi=2.0$. The absence of cool flame (1st stage ignition) is due to the relatively high octane rating (i.e. high resistance to self oxidize) of cyclohexane (RON 83, MON 77) and methylcyclohexane (RON 75, MON 71) comparing to those exhibiting two-stage ignition which have a typical octane rating around zero.

Figure 2-5 Typical heat release curve at autoignition for cyclohexane and methylcyclohexane. Condition: 900 rpm, $\phi=1.0$, C.R.=11.07, N2 dilution =100 SCFH, intake temperature =260 C.

It is found that the ignition temperatures of cyclohexane and methylcyclohexane are a weak function of equivalence ratio, as shown in **Figure 2-6**, similar to what was found for n-heptane in previous study. The ignition temperatures (T_{ig}) of the single stage

ignition of cyclohexane and methylcyclohexane are considerably higher than the first-stage T_{ig} of n-heptane, and slightly higher than second-stage T_{ig} of n-heptane.

Figure 2-6 Variation of ignition temperature of cyclohexane, methylcyclohexane and n-heptane with equivalence ratio

Gaseous species in engine exhaust is analyzed by an online Thermo-Electronic FT-IR spectrometer. **Figures 2-7** and **2-8** show early carbon monoxide is formed at low compression ratio, and as the compression ratio increases further, CO concentration decreases substantially with the increasing pressure and temperature until eventually takes off when approaching the autoignition. Both cyclohexane and methylcyclohexane display the similar behavior when the equivalence ratio is higher than certain value (cyclohexane $\phi \geq 1.0$, methylcyclohexane $\phi \geq 0.5$). At higher equivalence ratios, the decrease of CO concentration with the increasing compression ratio becomes less

significant, and a second increase in CO concentration with compression ratio is observed at $\phi=2.0$ for both compounds. This seemingly abnormal observation may be explained by the negative temperature coefficient (NTC) of the low temperature oxidation, where increasing temperature leads to slower reaction rate. In another word, although the two-stage ignition, the typical expression of the NTC, is not observed under this engine conditions, the negative temperature coefficient manifests itself in another way.

Figure 2-7 Variation of CO concentration with compression ratio in cyclohexane low temperature oxidation. Condition: 900 rpm, N₂ dilution =100 SCFH, intake temperature =260 C.

Figure 2-8 Variation of CO concentration with compression ratio in methylcyclohexane low temperature oxidation. Condition: 900 rpm, N₂ dilution =100 SCFH, intake temperature =260 C.

The engine exhaust is condensed and collected by using an ice bath. De-ionized water and dichloromethane are used to separate the collected sample into water layer which is discarded, and organic layer which is analyzed by GC-MS. Because of the absence of low temperature heat release in the model compound oxidation under the conditions used, no or little sample had been collected at the ice bath. The only exception is for the methylcyclohexane at $\phi=2.0$. Certain amount of liquid was collected at this equivalence ratio with compression ratio of 6.87 which is much less than that for ignition. **Figure 2-9** shows the GC-MS spectrum for this sample. The important compounds identified are listed in **Table 2-1**, among which almost all are oxygenated and cyclic species, especially cyclic ketones. The abundance of cyclic species indicates that the ring rupture seldom happens in the low temperature oxidation, in agreement with literature [2-

1, 2-2]. On the other hand, the presence of cyclohexane, cyclohexanone, and cyclohexenone suggests that dealkylation is an important pathway in methylcyclohexane low temperature oxidation, as suggested by Walker and Morley [2-3]. Classical low temperature oxidation mechanism can be applied to explain the formation of these species, but the correctness of such explanation remains to be questioned because few results if any have been published on the low temperature oxidation of methylcyclohexane. Further study is required to provide reasonable answers.

Figure 2-9 GC-MS spectrum of methylcyclohexane low temperature oxidation. Condition: 900 rpm, $\phi=2.0$, C.R.=6.87, N₂ dilution =100 SCFH, intake temperature =260 C.

Table 2-1 Compounds identified in the GC-MS spectrum of methycyclohexane oxidation

No.	Name	Formula	Structure
1	cyclohexane	C ₆ H ₁₂
2	5-hepten-2-one	C ₇ H ₁₂ O
3	cyclohexanone	C ₆ H ₁₀ O
4	2-cyclohexen-1-one	C ₆ H ₈ O
5	cyclohexanone, 3-methyl	C ₇ H ₁₂ O
6	1-cyclohexene-1-methanol	C ₇ H ₁₂ O
7	2-cyclohexen-1-one, 2-methyl (or 3-methyl)	C ₇ H ₁₀ O
8	1,2-cyclohexanediol, 1-methyl	C ₇ H ₁₄ O ₂

Subtask 2.2 Impact on Diesel Fuel Quality and Performance

Under this subtask, we continue to focus on two facility development activities, but have also made great strides in fuel and combustion characterization. One side of the facilities work has been refinement and enhancement of two existing engine test stands, one housing a Navistar V-8 7.3L turbodiesel engine and the other housing a DDC 4-cylinder 2.5L turbodiesel engine. The other activity has involved developing ignition testing capabilities which involved purchase of new IQT instrument and development of

an ignition test capability as an expansion of an existing CFR Octane Rating Engine (also reviewed under Subtask 2.1.3 for its use in gasoline studies).

2.2.1 Acquisition, Installation and Instrumentation of Ignition Test Equipment

At present, we are using the “IQT” ignition quality test instrument to examine the derived cetane number (DCN) of various diesel fuels, fuel blends and additized fuels. While we feel that there is room for improvement in the calibration of the IQT, it is giving reliable trends, measurements consistent with outside laboratories and useful data. We have begun tests on the impact of coal-derived compounds on the DCN of base diesel fuels.

In addition, a device to provide premixed prevaporized fuel samples to be fed to a CFR Octane Rating engine, operated with the spark plug deactivated, has been configured to serve as a “rapid compression machine” to study the elementary effects of fuel composition on the ignition process of hydrocarbons. Some preliminary data has been obtained for reference fuels and is presented below. **Figure 2-10** provides a sample of the type of data this experiment can provide. Here the ignition of n-heptane is examined, at fixed inlet temperature and equivalence ratio (0.05) and with increasing compression ratio. In **Figure 2-10(iii)** the first evidence of 1st stage ignition is observed at roughly 680 K. In **Figure 2-10(iv)**, 2nd stage ignition begins at roughly 800 K. These results are consistent with published experiments and numerical simulations of n-heptane ignition.

Figure 2-10 Ignition Process for n-Heptane at $\phi=0.05$ and Increasing Compression Ratio. In Plot (iii) the First Evidence of 1st Stage Ignition is observed at roughly 680 K. In Plot (iv), 2nd Stage Ignition Begins at roughly 800 K.

2.2.2. Development of Analytical Methods and Test Procedures

The “IQT” apparatus is now covered under an ASTM test method so that its operation and application are considered standard practice. We have agreed to participate in round robin testing activities to help support the community’s use of the IQT and to provide external comparison of our data.

The modification of the CFR Octane Rating engine to serve as a rapid compression machine for ignition studies represents a unique adaptation of a standard instrument and will provide a means of comparing experimental data with kinetic models of the ignition process.

2.2.3. Evaluation of Capabilities and Needs for Supplemental Measurements and Analyses

The analytical methods developed for the characterization of the fuel cuts from the PARC runs can now serve as the basis for subsequent fuel and SOF chemical analyses. We have developed procedures for use of an existing FTIR spectrometer to speciate the products of our ignition tests, which has already highlighted significant differences in the intermediate species present as we pass through first and second stage ignition for different fuels. We have also developed a plan for upgrading an existing gas chromatograph for hydrocarbon speciation from engine exhausts. We intend to perform the upgrade of the GC (from packed to capillary columns) and use a method that is the

same as in the Shimadzu GC-MS. This will allow the GC results to be interpreted through the species identification capabilities of the GC-MS.

2.2.4. Impact on Chemical and Physical Properties

The derived cetane number (DCN) for each of the fuel blends was measured in accordance with ASTM D6890-03a. A correlation has been developed to convert the measured ignition delay into a DCN, which is correlated with the CN measured by ASTM D613 (CFR Cetane Rating engine). The ignition delay (defined as the elapsed time from injection to where the chamber pressure reaches $P_{\text{initial}} + 50$ psi) under specified conditions was measured using the Ignition Quality Tester (IQT). The system is fully automated and an experiment consists of 15 pre-injections (to equilibrate system temperatures) followed by 32 injections. The reported DCNs are the average of these 32 injections of pre-filtered fuels.

Flash point was measured in accordance with ASTM D6450 using a MINIFLASH FLP fully automatic flash point tester. This tester utilizes the continuously closed cup (CCCFP) method. Values reported were based on the average of five measurements.

Kinematic Viscosity of the fuel blends was performed following ASTM method D-445-97 using a Cannon-Fenske Viscometer. Viscometer VE7 was loaded with 10 ml of sample fuel and immersed in the viscometer bath at 40°C. After allowing 20 minutes for the sample fuel temperature to equilibrate, the sample was forced into the test section of the viscometer using a pipette bulb. Time of flow was measured using a stopwatch with accuracy to 1/100 s. Five runs were performed per sample. Times(s) were

converted to kinematic viscosities (cSt) using a calibration with viscosity standard S3 (lot# 99101) from Cannon Certified Viscosity Standards.

The fundamental principle of the bulk modulus measurements as developed by O'Brien [2-4] is that under a sufficiently high pressure, a reduction in liquid volume occurs. The experimental approach used in this work yields a measurement for the isothermal bulk modulus of compressibility, B_T , whereas the isentropic bulk modulus, B_S , is more commonly reported. Although $B_T \neq B_S$ in general terms, the ratio B_S/B_T equals γ , the ratio of specific heats C_p/C_v , which is roughly unity for liquids such as water [2-5]. Furthermore, the difference between the specific heats $C_p - C_v$ equals $\alpha_p^2 v T B_T$, where α_p is the volume expansivity, and this product is very small for the substances of interest in this study [2-6]. Therefore, the distinction between the isentropic and isothermal bulk modulus of compressibility need not be maintained in the present context. The bulk modulus is calculated using equation (1), where B is the bulk modulus, P is the applied pressure, V_o is the volume of the sample at atmospheric pressure, and V is the volume of the sample at pressure P .

$$B = (P - P_o) * V_o / (V_o - V) \quad (1)$$

The sample was placed in a closed-bottom pycnometer, which was housed inside of a modified 21-R-30 Stainless Jerguson gage capable of handling pressures up to 4000 psi. The gage was equipped with quartz windows to allow for the observation of the sample height in the capillary of the pycnometer, which is etched with lines of a known height. The Jerguson gage was kept in a constant temperature bath (100°F) to ensure that

the measurement was isothermal. **Figure 2-11** depicts the Jerguson gage and pycnometer.

A compressed cylinder of helium was capable of providing the necessary pressure up to 1000 psi. For higher pressures a 4.5 L Aminco hydrogenation bomb was filled with helium and oil was pumped into the bomb using a pneumatically driven positive displacement pump. The oil compresses the helium, thereby increasing the pressure applied to the sample. This system is capable of delivering pressures up to 16,000 psi.

Chemical Composition

Figures 2-12 and 2-13 present the qualitative chromatograms from a petroleum-derived ultra low sulfur diesel (BP15) and a coal-derived diesel cut (EI-175), respectively. Total Ion Chromatograms (TIC) are shown for both fuels accompanied by Selected Ion Chromatograms (SIC) for prominent ions within the respective TICs. Compositional differences between the two fuels are obvious. Lighter compounds found at earlier retention times in the chromatogram of BP15 are absent with EI-175. Such compounds were likely converted during hydrotreatment, or distilled out in the gasoline and jet-fuel cuts.

BP15 was almost exclusively aliphatic in nature with chains ranging from C7 to C24. EI-175 contained only a few aliphatic compounds ranging from C14 to C21. Two and three-ringed aromatics comprised the bulk of EI-175. Most abundant were phenanthrene (m/z 178), and various isomers of its hydrogenated derivatives (m/z 158, 182, 192), as well as fluorene (m/z 166).

Production of coal-derived diesel was limited such that large quantities for testing were not available. Based on the above observations fluorene and phenanthrene were

chosen as readily available representatives of coal-derived diesel compounds. BP15 was used as a carrier fuel with fluorene and phenanthrene as dopants from 0.5 wt% to 5 wt%. These blends were then tested for DCN, flash point, viscosity, and bulk modulus. Results for these tests are presented in **Table 2-2** and **Figures 2-14** and **2-15**.

Fuel Properties

Addition of fluorene to BP15 decreased the DCN. As fluorene concentration in the petroleum-derived diesel was increased the DCN decreased. Phenanthrene addition to BP15 also decreased DCN. However, in contrast to fluorene, increasing the concentration of phenanthrene did not result in a continued decrease of DCN. Cetane number of a fuel indicates how easily it can be ignited under pressure and temperature in a combustion chamber. The higher the DCN the shorter the ignition delay which leads to less premixed combustion, lower peak cylinder pressure and lower NO_x formation [2-7]. Therefore the presence of fluorene, or phenanthrene, in a diesel fuel should increase the concentration of NO_x in the emissions.

Fluorene addition to ultra low-sulphur diesel fuel generally increased the flash point, however, at 0.5 wt% fluorene no change in the solutions flash point was measured compared to the baseline fuel. Increasing the concentration of fluorene in BP15 resulted in increasing flash point temperatures. At 0.5 wt% phenanthrene a slightly higher flash point was measured than that of BP15 alone. Further increases in phenanthrene concentration had little or no affect on the flash point of BP15. The most abundant single compound in BP15 was tetradecane (b.p. 252°C). Addition of fluorene (b.p. 298°C) and phenanthrene (b.p. 340°C) was sufficient to shift the affect of the lower molecular weight species in the diesel and increase the flash point.

Addition of either fluorene, or phenanthrene, had little or no affect on the kinematic viscosity of BP15. Addition of these aromatic compounds should not affect the spray characteristics of the diesel fuel.

Bulk modulus data for the fluorene and phenanthrene blends are presented as a function of pressure in **Figures 2-14** and **2-15**, respectively. Addition of either fluorene or phenanthrene to BP15 increased the bulk modulus, therefore reducing the compressibility of the fuel. In a pump-line-nozzle type fuel delivery system this reduction in compressibility could lead to advanced injection timing.

Coal-derived diesel was blended with BP15 at 5 wt%. DCN, flash point, viscosity, and bulk modulus measurements were taken for comparison with those of 5 wt% fluorene and 5 wt% phenanthrene (**Table 2-3** and **Figure 2-16**).

Flash point and DCN for 5 wt% EI-175 were comparable to that of 5 wt% fluorene, whereas the viscosity was slightly lower. Bulk modulus measurements for coal-derived diesel blends at 5 wt% were much lower than for either of the aromatic fuel blends and were only slightly higher than those for BP15 alone.

Hydroaromatics present in the coal-derived diesel have similar boiling points to fluorene (i.e. octahydrophenanthrene 295°C and perhydrophenanthrene 290°C). This fact alone may account for the similarities in flash point. However, apart from bulk modulus results, fluorene appears to provide sufficiently similar data as a substituted model compound. Bulk modulus results suggest a trend in compressibility: aromatics < hydroaromatics < aliphatics.

In summary, coal-derived diesel was high in hydroaromatics and aromatics. Attempts to simulate blends of coal-derived diesel in petroleum-derived diesel using

model compounds produced similar fuel properties for DCN, flash point and viscosity. Bulk modulus measurements for fluorene and phenanthrene fuel blends were similar, although much higher than that of the coal-derived diesel blend. Hydroaromatic content of the coal-derived diesel may be responsible for the difference in bulk modulus.

In future work under this task, engine studies will be performed to translate the fuel property differences into engine performance and emissions data. Hydroaromatic compounds, such as octahydrophenanthrene, will be investigated to ascertain their effect on fuel properties, particularly bulk modulus.

Figure 2-11 Bulk Modulus Testing Apparatus.

Figure 2-12 GCMS of BP15 Total Ion Chromatogram (TIC) and Selected Ion Chromatograms (SIC) of aliphatic fraction

Figure 2-13 GCMS of EI-175 TIC and SICs of major compounds

Table 2-2. Fuel Properties of BP15 Doped with Fluorene and Phenanthrene

Fuel	BP15	BP15/Fluorene				BP15/Phenanthrene			
Additive (wt%)	-	0.5	1	2	5	0.5	1	2	5
DCN	47.2	46.6	46.1	46.0	45.1	46.6	46.7	46.8	46.7
Flash Point (°C)	66.4	66.0	66.7	68.7	69.5	68.3	66.3	66.8	66.3
Smoke Point									
Viscosity (cSt)	2.5 ¹ 2.553 ²	2.492	2.507	2.497	2.519	2.500	2.492	2.530	2.528

1 Value taken from BP15 specification; 2 Measured value using Cannon-Fenske

Figure 2-14 Bulk modulus of BP15 doped with varying concentrations of fluorene

Figure 2-15 Bulk modulus of BP15 doped with varying concentrations of phenanthrene

Table 2-3. Fuel properties of coal-derived diesel EI-175

	BP15	5% F	5% P	5% EI-175
Additive (wt%)	-	5	5	5
DCN	47.2	45.1	46.7	44.9
Flash Point (°C)	66.4	69.5	66.3	69.0
Viscosity (cSt)	2.5 ¹ 2.553 ²	2.519	2.528	2.484

¹ Value taken from BP15 specification; ² Measured value using Cannon-Fenske

Figure 2-16 Bulk modulus coal-derived diesel compared to BP15 doped with fluorene and phenanthrene

2.2.5 Impact on CI Engine Emissions and Performance

Combustion and Efficiency Experiments

Experiments are being conducted in a DDC/VM 2.5L, 4-cylinder, turbocharged, intercooled, common-rail direct injection diesel engine. Detailed engine specifications are listed in **Table 2-4**. The engine setup is shown in **Figure 2-17**. Each cylinder of this engine has been instrumented with one AVL GU12P pressure transducer. Engine rail pressure has been monitored by an AVL SL31D-2000 high-pressure strain gauge pressure transducer. A hall-effect needle lift sensor provided by Wolff control has also been installed on this engine to obtain the needle lift trace on cylinder number 1 from the engine. An AVL 8-channel IndiModul system has been used as the data acquisition

system for this engine. An AVL 365C angle encoder has been installed on the engine together with the IndiModul system which enables 0.1 CA degree resolution acquisition of the signals. **Figure 2-18** is a direct exported diagram of the pressure traces for the cylinder pressures in all of the 4 cylinders from IndiModul. A Leeds & Northrup “Micromax” data acquisition system has been used to monitor the engine speed, torque, power, and several engine operating temperature and pressure parameters.

Table 2-4 Engine specification

Engine	DDC 2.5L TD DI-4V automotive diesel engine
Displacement	2.5L
Bore	92mm
Stroke	94mm
Compression Ratio	17.5
Connecting rod length	159mm
Rated Power	103KW@4000 RPM
Peak Torque	340Nm@1800 RPM
Injection system	Electronically controlled common-rail(Bosch)
Valve train	4 valves/cylinder

Figure 2-17 DDC/VM 2.5L common-rail diesel engine setup

Figure 2-18 Sample pressure traces from all of the 4 cylinders in the DDC 2.5L diesel engine

pressure trace has been obtained from IndiModul (**Figure 2-20**). Combustion analysis for apparent heat release rate (APHRR) (**Figure 2-21**) and bulk cylinder gas temperature (**Figure 2-22**) has been performed together with the analysis of brake specific fuel consumption (BSFC) (**Figure 2-23**).

Table 2-5 AVL 8-mode and brake mean effective pressure (BMEP)

Mode	Speed (rpm)	Load (ft.lb)	BMEP (MPa)
1	1000	0	0
2	1330	46.4875	0.32
3	1630	153.7641	1.05
4	1960	206.2452	1.41
5	4000	33.0984	0.23
6	3850	76.236	0.52
7	3850	131.7762	0.90
8	3670	189.6295	1.29

Figure 2-20 Cylinder pressure trace with different start of injections

Figure 2-21 Apparent heat release rate with different start of injections

Figure 2-22 Bulk cylinder gas temperature with different start of injections

Figure 2-23 Brake specific fuel consumption and thermo efficiency at different start of injections

As shown in **Figures 2-20** and **2-21**, the peak cylinder pressure reduced and the start of combustion retarded as the injection timing was retarded. When the injection timing was before the top dead center, premixed burned fraction followed the general decreasing trend. However, when the injection timing was retarded beyond TDC, the entire combustion process was represented as a big premixed spike and the peak heat released rate value increased as the injection timing was further retarded. Also, **Figure 2-24** shows that the maximum cylinder gas temperature was reduced as the injection timing was retarded.

Figure 2-24 Premixed burned fraction and maximum cylinder gas temperature at different start of injections

As the injection timing was retarded beyond the top dead center, the ignition delay would be considerably increased since the cylinder gas temperature began to reduce due to the fast expansion of the piston. Therefore, premixed phase combustion started to dominate the entire combustion process. The trade-off between brake specific fuel consumption and injection timing can be seen in **Figure 2-23**. As the injection timing was delayed, more fuel needed to be injected into the cylinder to produce the same expansion work as the one produce in the earliest injection timing. This increase of fuel consumption in turn leads to lower thermal efficiencies for the retarded injection timings.

At next stage of this project, detailed combustion and emissions analysis would be performed for coal derived diesel blends compared to baseline BP15 at different injection timings under selected modes from AVL 8-mode test cycle. It is also of particular

interest how will coal derived diesel fuel blends behave under low temperature premixed combustion mode in terms of the trade-off between BSFC (brake specific fuel consumption) and NO_x and the one between BSFC and soot emissions. Identified chemical compounds from coal derived diesel fuel will also be doped with baseline BP15 fuel to investigate how these compounds will affect the engine combustion and emissions at next stage.

For the purpose of better understanding the impact of the coal-derived compounds on the injection, ignition and combustion of diesel fuels in a practical engine, we have developed an installation of an existing AVL 513D Engine Videoscope (purchased under an NSF Research Equipment Grant, # CTS-0079073) in our Navistar V-8 7.3L turbodiesel engine. This required design and machining access for an endoscope probe and a light guide to visualize the fuel spray and the spray flame. The modified cylinder head is ready for use and will be implemented after some other preliminary emissions studies are completed.

Impact of Fuel Composition on Properties of Diesel Soot

This section of the report reports a comparison between BP15, 10%CDD, and 20%CDD. Emission data was obtained for BP15 and 20%CDD fuels. The oxidation behavior of the soot from engine combustion of BP15 and 10%CDD was determined by using the thermogravimetric and Differential Scanning Calorimetry (TGA-DSC). The engine used in this experiment is a single cylinder DI diesel engine operated at 75% load and 3600 rpm.

A highly instrumented, single-cylinder direct injection (DI) diesel engine with a maximum power output of 7 hp. Cylinder pressure and fuel-line pressures will be measured using Kistler piezoelectric pressure transducer models 6052B1 and 601B1,

respectively. A Hall-effect proximity sensor will be used to measure needle-lift in the injector. An AVL 364 shaft encoder installed on the engine crankshaft, along with a Keithley DAS 1800 data acquisition board enabled 0.1 CA degree resolutions of these signals. NOx emissions will be measured using an Eco-Physics NOx analyzer integral in an AVL GEM 110 emissions bench. The test fuels considered in this work are: an ultra low sulfur diesel with 15ppm sulfur content (BP15) and BP15 blended with 10% and 20% CDD.

In this study, the BP15 and 10% CDD soots were collected from the raw exhaust of a single-cylinder DI diesel engine. The soot oxidation behavior was conducted on the Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA-DSC provides data on soot mass reduction as a function of temperature and the oxidation temperature and time.

The preliminary investigations on the effects of the coal-derived diesel on engine emissions were conducted on the single-cylinder DI engine. The engine was operated at 75% load and 3600rpm. **Table 2-6** shows emission data for BP15 and 20%CDD. The injection of 20%CDD (-7.6 CA BTDC) is advanced relative to the BP15 fuel (-6.98 CA BTDC). As a result, the 20%CDD produce higher NOx than the BP15 fuel.

Figure 2-25 shows pressure data for BP15 and 20%CDD. BP15 has a relatively higher peak temperature. As seen in the heat release profile in **Figure 2-26**, the start of combustion is retarded for the 20%CDD relative to the BP15 fuel, due to the low cetane number of the 20%CDD fuel.

Table 2-6. Emission data for BP15 and 20%CDD

	BP15	20%CDD
NOx (ppm)	569	616
CO ₂ (%)	7.9	8.3
CO (ppm)	831	1060
UHC (ppm)	286	404

Figure 2-25 In-cylinder pressure data for BP15 and 20% CDD fuels.

Figure 2-26 Heat release profile for BP15 and 20% CDD fuels.

For temperature programmed oxidation (TPO) experiments, TGA-DSC tests were performed on a Q-600 thermogravimetric analyzer. Soot particles were collected from the raw exhaust of the single-cylinder DI diesel engine. The soot was collected on Teflo filters and then removed and heated at 500°C for 1 hour under nitrogen gas to remove the soluble organic fraction. Soot samples were then placed in TGA-DSC furnace and heated in air in the temperature range 20-700 °C using heating rate of 10 °C/min. **Figure 2-27** shows the mass reduction and heat release profiles as a function of temperature for BP15 and 10%CDD. It is obvious that the oxidation characteristics of the soot from both fuels are identical. This would indicate that the soot formation mechanisms and the physical/chemical properties of both soots are similar. **Table 2-7** shows some important thermal parameters of both soots.

Figure 2-27 TGA-DSC profiles for different soot samples.

Table 2-7. Thermal properties of diesel soot.

	BP15	10%CDD
*Onset temp. (°C)	525	519
Maximum peak temp. (°C)	627.65	630.43
Heat of reaction (kJ/g)	24.4	23.5

*T_{onset}: temperature at 5 wt.% weight loss

In future work, the impacts of engine operating conditions such as EGR, injection timing and injection strategies on soot oxidative reactivity will be evaluated. Bulk soot samples will be collected from the raw exhaust of the DDC engine. Further experiments will be conducted on the TGA-DSC to obtain the oxidation kinetics of diesel soot.

X-Ray Diffraction (XRD) will be used to obtain the interlayer spacing (d002) and the layer dimension (La). Raman Spectroscopy (RS) will be used to obtain the intensities of the amorphous and graphitic peaks and the intensity ratio will be interpreted as a measure of the in-plane crystallite dimensions. The density, pore size distribution, and active surface areas of different soots will also be determined. The CHN analyzer will be used to obtain information about the elemental composition of the soot. FTIR will provide data about the functional groups.

To gain better understanding about structural properties of diesel soot, TEM and HRTEM imaging will be obtained. These experiments will be conducted on JEOL 2010 LaB6 and on a field emission JEOL 2010F instruments located in the Material Research Institute (MRI) of Penn State. For TEM and HRTEM imaging, thermophoretic sampling unit will be used to capture soot particles from the raw exhaust. Soot particles will be collected on a 3 mm diameter copper grid coated with a lacey carbon film.

A Santoro-type diffusion flame will be used to assess the impacts of aromatics on soot reactivity by examining the role that the polyaromatic hydrocarbon (PAH) compounds play during the inception and growth stages of soot formation. Two aromatic compounds are of particular interest: Phenanthrene ($C_{14}H_{10}$) and fullerene ($C_{13}H_{10}$). These compounds will be heated in a vaporizer to temperatures above the respective melting points, and their vapors will be entrained into the flowing burner fuel (ethylene). Soot will then be collected from the resulting sooting flame.

Task 3. Desulfurization, Denitrogenation, Saturation of Aromatics, Chemicals from Coal

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Subtask 3.1: Desulfurization and Denitrogenation

Ultra-deep hydrodesulfurization (HDS) of diesel fuel has become an important research area because of increasingly stringent environmental regulations on sulfur content in fuel [3-1]. The diesel containing high sulfur compounds leads to higher level of SO_x in the exhaust, which results in acid rain and poisons catalysts in catalytic converters for reducing CO and NO_x [3-2]. Consequently, the sulfur level in diesel fuel must be reduced from the present 500 ppmw to 15 ppmw by 2006 in the US. Therefore, many studies on deep hydrodesulfurization of model and real diesel fuels are being conducted with various methods and different catalysts by many research groups [3-1, 3-3~3-8].

Hydrodesulfurization is currently a major process in petroleum refineries to reduce the sulfur in the liquid hydrocarbon fuels. However, it was found by many researchers that the nitrogen compounds coexisting in middle–distillate oil inhibit the deep hydrodesulfurization and the removal of such nitrogen compounds from the middle–distillate oil can improve significantly the deep hydrodesulfurization performance [3-3, 3-4, 3-9]. Recently, a new process, called PSU-SARS, is being explored in our laboratory. The idea in this process is to remove sulfur in the fuels by selective adsorption. The major advantages of this process are that the process can run at ambient temperature and pressure without using hydrogen gas and the spent adsorbents can be regenerated either by solvent washing or by oxidation using air. The idea in PSU-SARS process can be also applied to pre-denitrogenation of the middle–distillate oil to improve the deep hydrodesulfurization performance.

In this study, initially, we are focusing on the adsorptive denitrogenation of basic or very reactive nitrogen compounds such as quinoline or indole, which influences very much on hydrodesulfurization. It is expected that these nitrogen compounds may be removed easily by adsorption as compared with sulfur compounds because they are much more reactive than sulfur compounds in hydrotreating process. Therefore, the performance of hydrodesulfurization may be improved, even though basic or reactive nitrogen compounds are removed from middle-distillate oil. Since this adsorption technique is attracting more attentions in academics as well as industries, the fundamental research for adsorption properties of sulfur and nitrogen compounds on adsorbent is still being required while the main issue in this research is to increase the adsorption capacity of adsorbent for the requirement of industry.

3.1.1. Experimental

3.1.1.1. Adsorptive desulfurization and denitrogenation

In order to investigate adsorption properties of aromatic, sulfur and nitrogen compounds over different adsorbents, adsorptive denitrogenation/desulfurization was performed in flow system and collected samples by adsorption were analyzed by Antek total S/N analyzer and GC-FID. On adsorptive denitrogenation in flow system, a model fuel containing 152 ppmw of N as quinoline and 151 ppmw of N as indole in the mixture solvent of decane and hexadecane was used in this study. The total nitrogen concentration in the fuel was 303 ppmw. Total sulfur concentration was 686 ppmw of S as same amount of DBT and 4,6-DMDBT. **Table 3-1** shows the composition of model fuel for adsorptive denitrogenation in flow system.

Table 3-1 The concentration of each compound in model fuel

Chemicals	Concentration		Molar concentration (mmol/kg)
	(wt %)	ppmw S or N	
Sulfur compounds			
DBT(99+%)	0.20	343.3	10.7
4,6-DMDBT(97%)	0.23	343.4	10.7
Total		686.7	
Nitrogen compounds			
Quinoline	0.14	152.0	10.8
Indole	0.13	151.0	10.8
Total		303.0	
Aromatics			
Naphthalene	0.14		10.7
1-Methylnaphthalene	0.15		10.7
tert-Butylbenzene	9.92		
Total	10.21		
Paraffins			
n-Decane	44.01		
n-Hexadecane (99+%)	44.02		
n-Tetradecane (99+%)	0.06	(Internal standard)	
Total	100.00		

According to the results of adsorptive denitrogenation in the batch system in our previous report, zeolite supported Cu and CuCe adsorbents were selected and Ag/Y-zeolite was also chosen because it has been reported that Ag adsorbs aromatic compounds through π -complexation, which is one of the important adsorption factors. These zeolite-based adsorbents were pretreated with He flow at 350°C for 1 h for the reduction of metal before adsorptive denitrogenation/desulfurization.

Also, activated alumina and activated carbon which are used widely for adsorption process in industries were tested. The activated alumina was purchased from Aldrich Chemical Co. and has surface area of 173 m²/g and pore size of 59.4 Å. In general, activated alumina is used for removing nitrogen compounds and polar compounds in real fuels and is expected to show good adsorption properties of nitrogen compounds in the

model fuel. The activated carbon was provided from Westvaco and has surface area of 1843 m²/g and pore size of 28.6 Å. Both adsorbents were pretreated with nitrogen flow at 200 °C for 1 h in order to remove water adsorbed in their surface which might significantly influence the adsorption properties. Also, A-5 (Ni/Si-Al) adsorbents, which were developed in our lab, was tested and compared with other adsorbents. **Table 3-2** shows the surface area, pore volume and pore diameter of zeolite-based adsorbents, nickel-based adsorbent, activated alumina and activated carbon measured by N₂ adsorption (ASAP2010, Micromeritics).

Table 3-2 Properties of zeolite-based adsorbents, activated alumina and activated carbon

	Surface Area m ² /g	Pore Volume cm ³ /g	Pore diameter (Å)
Cu/Y-zeolite	584	0.0	~7.4
CuCe/Y-zeolite	383	0.1	~7.4
Ag/Y-zeolite	273	0.1	~7.4
A-5 (Ni/SiO ₂ -Al ₂ O ₃)	157	-	-
Activated carbon	1843	1.2	28.6
Activated alumina	173	0.3	59.4

These adsorbents were pretreated with H₂ flow at 200°C for 1 h and cooled down to room temperature. The adsorptive denitrogenation of the model fuel on all adsorbents was performed in a flow system at room temperature with LHSV of 4.8 h⁻¹. Analysis of fuel samples was conducted using Antek 9000 series nitrogen and sulfur analyzer for more

accurate quantitative analysis and also SRI GC equipped with a capillary column (XTI-5, Restek) and a flame ionized detector (FID) for identification of each compound.

The adsorption of light cycle oil (LCO, EI-163 from United Refinery) was also performed at the same conditions as the adsorption of model fuels. The LCO used in this project contains 1.5wt% S and 464 ppmw N with a lot of aromatic compounds. The sulfur concentration was much higher than that (687 ppmw S) in the model fuel, while the nitrogen concentration was similar to that (303 ppmw N) in the latter.

3.1.1.2. Hydrodesulfurization of 4,6-DMDBT

The reactant chemicals, 4,6-DMDBT and decahydronaphthalene (decalin, used as solvent), were obtained from Aldrich Chemical Co., and were used without further purification. For the HDS of 4,6-DMDBT, its concentration was 1.23 wt% (0.81 mol%) in decalin.

HDS was carried out in a batch reactor with a volume of 25 ml. The reactor was loaded with 0.1 g catalyst and 4.0 g decalin fuel containing 4,6-DMDBT, and was then purged with nitrogen and hydrogen five times, respectively, before being pressurized with hydrogen to 300 psi. The reactor was placed in a fluidized sand bath, which was preheated to 300, 325 or 350°C, and was agitated at 200 strokes/min. The temperature inside the reactor was monitored by a thermocouple. Following the reaction, the reactor was removed from the sand bath and was immediately quenched in a cold-water bath. A GC-MS (Shimadzu GC17A/QP-500) was used for identification of the products, while a gas chromatograph (SRI 8610C), equipped with an FID, was used for quantitative analysis of products.

To improve the HDS of 4,6-DMDBT, several NiMo and CoMo sulfide and Ni phosphide catalysts were prepared with high or low metal loadings. High metal loaded NiMo and CoMo catalysts were prepared on mesoporous molecular sieve MCM-41 through a wet co-impregnation method. After the impregnation, the catalysts were dried at 80°C overnight in an oven and then the catalysts were calcined at 500°C for 5 h. The final catalysts contain 27 wt% MoO₃ and 6 wt% NiO or CoO. Another high metal loaded NiMo and CoMo/MCM-41 catalysts were prepared with a chelating agent, nitrilotriacetic acid (NTA), in ammonium hydroxide. It was reported that NTA might help interaction Mo and Ni or Co to MCM-41 support in impregnation. Ammonium molybdate and nickel nitrate were dissolved in the solution and impregnated on MCM-41. Then the catalysts were dried at 110°C, but not calcined before presulfidation. Low metal loaded NiMo and CoMo catalysts were prepared on CeO₂ (Rhodia) with a wet co-impregnation method. After the impregnation, the catalysts were dried at 110°C overnight in an oven and then calcined at 500°C for 5 h. The final catalyst contains 14 wt% MoO₃ and 3 wt% NiO. The NiMo and CoMo catalysts were presulfided at 350°C for 6 h in a flow of 5 vol % H₂S-H₂ at a flow rate of 150 ml/min and were subsequently stored in decalin to minimize oxidation. In addition, Ni phosphides supported on Al₂O₃, CeO₂ and MCM-41 were prepared with impregnation of nickel nitrate and ammonium phosphate. After the impregnation, the catalysts were dried at 80°C overnight and then calcined at 500°C for 5 h. To obtain final Ni phosphide, the catalysts were reduced in H₂ flow with a temperature programmed method at low ramping rate (1°C/min) by 550°C and then 2 h maintenance at 550°C. After the reduction, the phosphide catalysts were also stored in decalin to minimize oxidation.

3.1.2. Results and discussion

3.1.2.1. Adsorption on Zeolite-based Adsorbent

The breakthrough curves of the six adsorbates, Nap, 1-MNap, 4,6-DMDBT, DBT, quinoline and indole, over Cu, CuCe and Ag/Y-zeolite adsorbents at 25°C and 4.8 h⁻¹ LHSV are shown in **Figures 3-1~3-3**. For the Cu/Y-zeolite adsorbent, the aromatic and sulfur compounds had almost same breakthrough and their breakthrough amount was 1.0 gram of the treated fuel per gram of adsorbent (g-F/g-A). The breakthrough of nitrogen compounds was later than other compounds and the breakthrough amount of treated fuel was 2.2 g-F/g-A for indole and 3.4 g-F/g-A for quinoline. For the CuCe/Y-zeolite adsorbent, the breakthrough of aromatic and sulfur compounds showed very similar and their breakthrough amount of treated fuel was 3.4 g-F/g-A. Therefore, the addition of Ce on Cu/Y-zeolite increased the capacity of aromatic and sulfur compounds. As the breakthrough of nitrogen compounds, the Ce addition did not affect the breakthrough amount of quinoline while the breakthrough amount of indole increased little. According to the breakthrough order, the adsorptive selectivity for the six adsorbates over Cu and CuCe/Y-zeolite can be represented by the order of Nap $\approx$ 1-MNap $\approx$ 4,6-DMDBT $\approx$ DBT < indole $\leq$ quinoline. The breakthrough and saturate capacities for each adsorbate were calculated and listed in **Table 3-3**. In order to facilitate the quantitative discussion of the adsorptive selectivity, a relative selectivity factor was used in the present study, which was defined as:

$$\alpha_{i-n} = \text{Cap}_i / \text{Cap}_n \quad (1)$$

where, Cap_i is the adsorptive capacity of compound i corresponding to the breakthrough point and Cap_n is the adsorptive capacity of the reference compound, Nap, corresponding to its breakthrough point. It should mention that as using the kinetics breakthrough capacities instead of the equilibrium capacity in equation 1, the defined selectivity factor is not for the equilibrium selectivity. The calculated relative selectivity factor on the basis of the breakthrough curves are tabulated as shown in **Table 3-4**. α_{i-n} value for Cu/Y-zeolite is 1.0, 1.0, 1.0, 1.0, 2.2 and 3.5, and the value for CuCe/Y-zeolite is 1.0, 1.0, 1.0, 0.9, 1.2 and 1.3, respectively, for Nap, 1-MNap, 4,6-DMDBT, DBT, quinoline and indole.

Figure 3-1 The breakthrough of aromatic, sulfur and nitrogen compounds over Cu/Y-zeolite.

Figure 3-2 The breakthrough of aromatic, sulfur and nitrogen compounds over CuCe/Y-zeolite

Table 3-3 The breakthrough and saturate capacity of each compound in model fuel for different adsorbents

Adsorptive capacity (mmol/g)		Nap	1-MNap	DBT	DMDBT	Indole	Quinoline
Cu/Y-zeolite	Breakthrough	0.011	0.011	0.011	0.011	0.024	0.037
	Saturate	0.022	0.018	0.020	0.017	0.032	0.057
CuCe/Y-zeolite	Breakthrough	0.036	0.036	0.036	0.034	0.044	0.047
	Saturate	0.038	0.035	0.038	0.033	0.044	0.055
Ag/Y-zeolite	Breakthrough	0.007	0.007	0.007	0.007	0.037	0.052
	Saturate	0.014	0.010	0.011	0.008	0.044	0.067
Ni/SiO ₂ -Al ₂ O ₃	Breakthrough	0.017	0.017	0.052	0.039	0.167	0.125
	Saturate	0.022	0.021	0.070	0.043	0.186	0.151
Activated alumina	Breakthrough	0.015	0.015	0.024	0.033	0.195	0.251
	Saturate	0.019	0.020	0.040	0.038	0.227	0.289
Activated carbon	Breakthrough	0.066	0.089	0.202	0.295	0.705	0.536
	Saturate	0.091	0.105	0.252	0.336	0.732	0.579

Table 3-4 The selectivity of each compound in model fuel for different adsorbents

Selectivity ¹	Nap	1-MNap	DBT	DMDBT	Indole	Quinoline
Cu/Y-zeolite	1.0	1.0	1.0	1.0	2.2	3.5
CuCe/Y-zeolite	1.0	1.0	1.0	0.9	1.2	1.3
Ag/Y-zeolite	1.0	1.0	1.0	1.0	5.0	7.0
Ni/SiO ₂ -Al ₂ O ₃	1.0	1.0	3.1	2.0	10.1	7.6
Activated alumina	1.0	1.0	2.2	2.2	12.8	16.5
Activated carbon	1.0	1.3	3.0	4.5	10.6	8.1

¹Selectivity is the capacity ratio of each compound to naphthalene

On the Ag/Y-zeolite adsorbent, the breakthrough of aromatic and sulfur compounds was similar and their breakthrough amount of treated fuel was 0.7 g-F/g-A. The breakthrough of quinoline was later than that of indole. The breakthrough amount of nitrogen compounds was 3.5 g-F/g-A for indole and 4.1 g-F/g-A for quinoline. According to the breakthrough order, the adsorptive selectivity for the six adsorbates over Ag/Y-zeolite can be represented by the order of Nap $\approx$ 1-MNap $\approx$ 4,6-DMDBT $\approx$ DBT < indole < quinoline. The relative selectivity factor on the basis of the breakthrough curves, α_{i-n} value, on Ag/Y-zeolite is 1.0, 1.0, 1.0, 1.0, 5.0 and 7.0, respectively, for Nap, 1-MNap, 4,6-DMDBT, DBT, quinoline and indole.

Figure 3-3 The breakthrough of aromatic, sulfur and nitrogen compounds over Ag/Y-zeolite.

3.1.2.2. Adsorption on Nickel-based Adsorbent

The breakthrough curves of the six adsorbates, Nap, 1-MNap, 4,6-DMDBT, DBT, quinoline and indole, over A-5 (Ni/SiO₂-Al₂O₃) at 25 °C and 4.8 h⁻¹ LHSV are shown in **Figure 3-4**. The first two breakthrough compounds were Nap and 1-MNap, with almost the same breakthrough amount of the treated fuel, 1.6 g-F/g-A. After breakthrough, the C/C₀ value (a ratio of the outlet concentration to the initial concentration in the model fuel) for the two aromatics increased sharply to over 1.0. The third breakthrough compound was 4,6-DMDBT with the breakthrough amount of the treated fuel of 3.2 g-F/g-A. Interestingly, DBT broke through at an amount of the treated fuel of 4.9 g-F/g-A, the breakthrough amount of the treated fuel was about 1.6 times higher than that for 4,6-DMDBT. The amount of the treated fuel corresponding to the saturated point was 4.9 and

8.7 g-F/g-A, respectively, for 4,6-DMDBT and DBT. After saturate point, the C/C_o value for 4,6-DMDBT rose sharply until $C/C_o = 1.4$, while the C/C_o value for DBT increased gradually to 1.16. This phenomenon was not shown in the breakthrough of aromatic and sulfur compounds on zeolite-based adsorbents. Quinoline and indole broke through at the treated-fuel amount of 11.6 and 15.5 g-F/g-A, respectively. According to the breakthrough order, the adsorptive selectivity for the six adsorbates over A-5 can be represented by the order of $\text{Nap} \approx 1\text{-MNap} < 4,6\text{-DMDBT} < \text{DBT} < \text{quinoline} < \text{indole}$. The relative selectivity factor on the basis of the breakthrough curves, α_{i-n} value is 1.0, 1.0, 2.0, 3.1, 6.2, and 10.1, respectively, for Nap, 1-MNap, 4,6-DMDBT, DBT, quinoline and indole as shown in **Table 3-4**. Based on the selectivity of DBT and DMDBT, the nickel-based adsorbent is good for selective removal of the sulfur compounds without the steric hindrance from hydrocarbon stream, such as gasoline, kerosene and jet fuel. The adsorbent seems to have the direct interaction between the heteroatom in the adsorbate and the surface nickel.

Figure 3-4 The breakthrough of aromatic, sulfur and nitrogen compounds over A-5.

3.1.2.3. Adsorption on Activated Alumina

The breakthrough curves of the six adsorbates over the activated alumina at 25°C and 4.8 h⁻¹ LHSV are shown in **Figure 3-5**. Both Nap and 1-MNap broke through at the treated-fuel amount of 1.4 g-F/g-A. After the breakthrough point, the C/C_0 value for the two aromatics rose sharply to about 1.4 and then returned to 1.0 when the column was saturated by DBT and 4,6-DMDBT. 4,6-DMDBT and DBT broke through with almost the same breakthrough treated-fuel amount (3.1 g-F/g-A). After the breakthrough, the C/C_0 values increased synchronously to around 1.15, and then, stayed at this value until indole broke through. The C/C_0 values for the two sulfur compounds decreased gradually to 1.0 when the adsorbent was saturated by indole. Indole broke through at an amount of the treated fuel of 18.9 g-F/g-A. After the breakthrough, the C/C_0 value of indole increased to 1.17, and then, returned to 1.0 when the adsorbent was saturated by

quinoline. The last breakthrough compounds was quinoline with the breakthrough treated-fuel amount of 23.2 g-F/g-A, and the amount of treated fuel corresponding to saturate point was 31.1 g-F/g-A. The breakthrough and saturate capacities for each adsorbate were calculated and listed in **Table 3-3**. The adsorptive selectivity for the six adsorbates over the activated alumina increased in the order of naphthalene $\approx$ 1-methylnaphthalene < 4,6-DMDBT $\approx$ DBT $\ll$ indole < quinoline. The relative selectivity factor (α_{i-n}) was 1.0, 1.0, 2.2, 2.2, 12.8, and 16.5 for Nap, 1-MNap, 4,6-DMDBT, DBT, indole and quinoline.

Figure 3-5 The breakthrough of aromatic, sulfur and nitrogen compounds over activated alumina.

The activated alumina was activated to be acidic and that kind of alumina is used widely to remove polar compounds and nitrogen compounds which have unpaired electrons on

nitrogen atom. Therefore, the adsorption selectivity on the activated alumina depends on the polarity and the acidic-basic interaction. The activated alumina is very good for selective separation of nitrogen compounds, especially for basic nitrogen compounds, but not very successful for separating the sulfur compounds from hydrocarbons.

3.1.2.4. Adsorption on Activated Carbon

The breakthrough curves over the activated carbon at 25°C and 4.8 h⁻¹ LHSV are shown in **Figure 3-6**. Nap broke through at a treated-fuel amount of 6.2 g-F/g-A. After the breakthrough, the C/C₀ value for Nap rose sharply to over 1.4, and then, returned to 1.0 gradually at the treated-fuel amount of 30 g-F/g-A. 1-MNap broke through at a treated-fuel amount of 8.4 g-F/g-A, and then, the C/C₀ value increased sharply to over 1.3. The breakthrough amount of the treated fuel for DBT was 19 g-F/g-A. After that the C/C₀ values for DBT increased sharply to around 1.4, and then, stayed at this value until the column was saturated by 4,6-DMDBT. 4,6-DMDBT broke through with a treated-fuel amount of 27.6 g-F/g-A, and then, increased sharply to over 1.2. The C/C₀ value for the two sulfur compounds decreased gradually to 1.0 when the column was saturated by indole. The breakthrough amount of the treated fuel for quinoline and indole was 49.3 and 66.1 g-F/g-A, respectively, and the saturated amount of the treated fuel was 60.3 and 86.7 g-F/g-A, respectively. The corresponding breakthrough and saturate capacities for each adsorbate are listed in **Table 3-3**. The adsorptive selectivity for the six adsorbates over the activated carbon increased in the order of Nap < 1-MNap < 4,6-DMDBT < DBT < quinoline < indole. The relative selectivity factor (α_{i-n}) was 1.0, 1.3, 3.0, 4.5, 8.1, and 10.6 for Nap, 1-MNap, DBT, 4,6-DMDBT, quinoline and indole, as shown in **Table 3-4**.

The activated carbon shows higher adsorptive capacity and selectivity for sulfur and nitrogen compounds, especially for the sulfur compounds with methyl groups, such as 4,6-DMDBT as compared with other adsorbents. In this study, the activated carbon was the best adsorbent for removing sulfur compounds as well as nitrogen compounds.

Figure 3-6 The breakthrough of aromatic, sulfur and nitrogen compounds over activated carbon.

3.1.2.1.5. Adsorption of LCO on Activated Carbon

The adsorption of LCO (light cycle oil) was performed at 25°C and 4.8 h⁻¹ LHSV on the activated carbon which showed excellent adsorption properties of the model fuel and very high adsorption capacity of sulfur and nitrogen compounds. The LCO used in this study contains 1.5 wt% S (15000 ppmw S) and 464 ppmw N. **Figure 3-7** shows the breakthrough of sulfur and nitrogen. The breakthrough of sulfur was very early and even the first collected sample contained 2878 ppmw S while it did not contain nitrogen at all.

The breakthrough amount of the treated fuel for sulfur was less than 1.3 g-F/g-A, and the C/C_0 values for sulfur increased sharply to around 1.0 after the breakthrough. Nitrogen concentration broke through with a treated-fuel amount of 4.9 g-F/g-A. Then, the C/C_0 value increased sharply to 0.8 and then slowly to 1.0 until the breakthrough amount up to 45 g-F/g-A. **Table 3-5** shows the breakthrough amount of sulfur and nitrogen in the adsorption of LCO. The breakthrough capacity for sulfur was very similar to that for model fuel (0.497 mmol/g-A). It means that most of the sulfur compounds in LCO may be DBTs (DBT and 4,6-DMDBT). However, the breakthrough amount of treated fuel was much less in the adsorption of LCO than in the adsorption of model fuel because LCO contains very higher sulfur concentration. The breakthrough capacity for nitrogen was 0.162 mmol/g-A and much lower than that in the adsorption of model fuel (1.241 mmol/g-A). It may be because the LCO contains very high concentration of aromatic compounds, some of which, specifically poly condensed aromatic compounds, significantly affect on the adsorption of nitrogen. Also, it contains different kinds of nitrogen compounds, some of which may hardly adsorb on activated carbon. In the LCO, there might be some non-basic nitrogen compounds, carbazole-type nitrogen compounds which have very low reactivity and adsorption affinity to adsorbents or catalysts. If the LCO contains both non-basic nitrogen compounds and basic nitrogen compounds, quinoline-type nitrogen compounds, the former nitrogen compounds may break through earlier than basic nitrogen compounds. This results in the breakthrough of nitrogen until 0.8 of C/C_0 and then the latter nitrogen compounds adsorb more on the activated carbon until the saturation of nitrogen compounds. Therefore, it is necessary to investigate the

effect of non-basic nitrogen compounds on the adsorption of LCO. For this, first, LCO need to be analyzed in detail with GC-PFPD, GC-MS or analysis instruments.

Figure 3-7. The breakthrough of sulfur and nitrogen in LCO over activated carbon.

Table 3-5. The breakthrough and saturate capacity of sulfur and nitrogen in LCO on activated carbon by Antek total S/N analyzer

Capacity (mmol/g-A)	Sulfur	Nitrogen
Breakthrough	< 0.497	0.162
Saturate	0.869	0.357

3.1.2.6. Hydrodesulfurization of 4,6-DMDBT

To develop deep HDS catalysts, several NiMo, CoMo and Ni phosphide catalysts were prepared. The prepared NiMo/MCM-41 catalyst contains 27 wt% MoO₃ and 6 wt% NiO, which are higher metal amount as compared with a commercial CoMo and NiMo catalysts which contain 14 wt% MoO₃ and 3 wt% NiO or CoO. The MCM 41 support which was prepared with SiO₂/Al₂O₃ ratio of 50 in our laboratory has around 1000 m²/g and higher pore volume 1.33 ml/g, which is much higher than those of Al₂O₃. So, the high amount of Ni and Mo metals was able to be loaded on the MCM-41 support. In the first year, we tried to prepare NiMo and CoMo catalysts supported on MCM-41, but their results were not enough to be attractive. At that time, the catalysts were prepared with incipient wetness impregnation, which might be affected by the acidity of MCM-41 support. Therefore, wet impregnation with enough water was employed this year to prepared NiMo and CoMo catalysts on MCM-41 support and other supports (CeO₂ and Al₂O₃). **Tables 3-6 ~ 3-8** and **Figures 3-8 ~ 3-10** show the conversion of 4,6-DMDBT and the selectivity of products over the catalysts prepared in this study after HDS of 4,6-DMDBT under the reaction conditions with 300°C, 325°C or 350°C and 300 psi of H₂ pressure for 30 min.

High metal loaded NiMo and CoMo/MCM-41 catalyst shows high activity of 4,6-DMDBT at 300 and 325°C. Specifically, NiMo/MCM-41 has higher HDS activity than other catalysts and even higher than commercial NiMo catalyst (Cr424) which contains 14wt% MoO₃ and 3wt% NiO on alumina before sulfidation. The conversion of 4,6-DMDBT over the NiMo/MCM-41 was 28% and 36% at 300 and 325°C, respectively and it is much higher than that over the commercial catalyst, which was 18% and 33%,

respectively. CoMo/MCM-41 catalysts also showed high activity at those temperatures and the conversion was 19% and 32%, respectively. Therefore, wet co-impregnation improved the HDS activity of NiMo and CoMo/MCM-41 catalysts as compared with the same catalysts prepared by incipient wetness impregnation in first year. It may be because the acidity of MCM-41 support was affected by water solution and preparation method. In the case of incipient wetness impregnation, small amount of solution of Mo and/or Ni (or Co) is dripped in solid support and penetrated immediate inside pore. The metals in small amount water may have strong interaction with high acidic support. In the case of wet impregnation, however, the metals are dissolved in enough water and the metals' mobility may be high on even acidic support. Then their dispersion will be increased.

In the HDS of 4,6-DMDBT at high temperature, e.g., 350°C, the conversion of 4,6-DMDBT over NiMo and CoMo/ MCM-41 catalysts increased to 42% and 39%, respectively. But they were lower than the commercial catalyst over which the conversion was 47%. NiMo and CoMo/MCM-41 prepared with NTA (hereafter NiMo-NTA and CoMo-NTA) and supported on CeO₂ showed pretty good HDS activity although the conversions over them were not higher than the commercial catalyst. The conversion was 14% and 11% over NiMo-NTA and CoMo-NTA and 15% and 12% over NiMo and CoMo/CeO₂, respectively at 300°C. The conversion increased with increasing temperature. Interestingly, NiMo-NTA catalyst has very high HDS/DDS ratio of around 15, which was simply calculated with the sum of hydrogenated products (HDMDBT, MCHT and DMBCH) and direct desulfurized product (DMBP).

In the product distribution, only NiMo/MCM-41 had isomerized DMDBT (dimethyldibenzothiophen) at 300°C, which was produced after one or two methyl-group moved to other position in benzene ring from 4- and 6- position, but could not be identified by GC-FID and GC/MS. At higher temperatures, the isomerized products were increased and detected on all NiMo and CoMo catalysts while the HYD/DDS ratio decreased significantly. 4,6-DMDBT has two methyl group at 4- and 6- positions, which may hinder the direct adsorption of sulfur atom in DBT to catalytic active site. When one or two methyl groups move to other position, the DMDBT has less steric hindrance by methyl group and may be converted easily to DMBP through DDS pathway. This results in lower HYD/DDS ratio while the selectivity of DMBP increased.

Supported Ni phosphide catalysts were also tested at the same conditions as the NiMo and CoMo catalysts were. They had lower activity than the latter catalysts and did not produce isomerized DMDBT at all temperature range tested in this study, but showed different activity and selectivity in dependence on supports. Ni₂P/MCM-41 had higher activity than the other phosphide catalysts and Ni₂P/Al₂O₃ had very higher HYD/DDS ratio while CeO₂ supported Ni phosphide has lower the ratio.

Based on the results, high metal loaded NiMo/MCM-41 catalyst had higher activity of 4,6-DMDBT HDS at 300 and 325°C than other catalysts tested in this project. At 350°C, however, the commercial NiMo catalyst had higher activity. Therefore, MCM-41 supported sulfide catalysts which had higher activity than others might be promising deep HDS catalysts after they are investigated further and improved.

Table 3-6. The conversion and selectivity of products over the catalysts prepared after HDS of 4,6-DMDBT at 300°C and 300 psi of H₂ pressure

Catalyst	Conv. (%)	Selectivity (%)					HYD/DDS ¹
		HDMDBT	DMBP	MCHT	DMBCH	Isomer	
NiMoS/Al ₂ O ₃ (Cr424)	17.8	39.8	9.6	44.5	6.2	0.0	9.43
6%NiO 27%MoO ₃ /MCM-41	28.2	66.3	11.3	9.6	5.8	7.0	7.20
6%CoO 27%MoO ₃ /MCM-41	19.2	58.4	15.0	15.5	11.0	0.0	5.65
6%NiO 27%MoO ₃ -NTA /MCM-41	14.3	67.6	6.2	20.0	6.2	0.0	15.02
6%CoO 27%MoO ₃ -NTA/MCM-41	10.6	47.9	34.3	11.1	6.6	0.0	1.91
3%NiO 14%MoO ₃ /CeO ₂ (Rhoida)	15.4	59.6	20.0	16.1	4.4	0.0	4.00
3%CoO 14%MoO ₃ /CeO ₂ (Rhoida)	11.5	57.2	32.1	5.1	5.6	0.0	2.11
Ni ₂ P/MCM-41	8.1	50.9	17.8	27.3	3.9	0.0	4.61
Ni ₂ P/CeO ₂	5.1	36.7	48.7	8.3	6.3	0.0	1.05
Ni ₂ P/Al ₂ O ₃	7.1	62.0	9.7	23.2	5.1	0.0	9.31

¹HYD/DDS = [HDMDBT+MCHT+DMBCH]/[DMBP]

Figure 3-8. The conversion and selectivity of products over the catalysts prepared after HDS of 4,6-DMDBT at 300°C and 300 psi of H₂ pressure.

Table 3-7. The conversion and selectivity of products over the catalysts prepared

after HDS of 4,6-DMDBT at 325°C and 300 psi of H₂ pressure

Catalyst	Conv. (%)	Selectivity (%)					HYD/DDS ¹
		HDMDBT	DMBP	MCHT	DMBCH	Isomer	
NiMoS/Al ₂ O ₃ (Cr424)	32.8	26.2	17.6	43.0	7.0	6.2	4.34
6%NiO 27%MoO ₃ /MCM-41	36.4	40.2	30.4	7.9	3.8	17.7	1.71
6%CoO 27%MoO ₃ /MCM-41	32.3	35.9	24.5	7.7	6.6	25.2	2.05
6%NiO 27%MoO ₃ -NTA /MCM-41	24.9	39.2	17.1	39.5	4.2	0.0	4.84
6%CoO 27%MoO ₃ -NTA/MCM-41	13.6	34.9	26.9	35.2	3.0	0.0	2.71
3%NiO 14%MoO ₃ /CeO ₂ (Rhoida)	19.3	54.0	5.5	28.9	8.0	3.6	16.56
3%CoO 14%MoO ₃ /CeO ₂ (Rhoida)	18.0	59.5	9.9	17.3	5.2	8.1	8.28
Ni ₂ P/MCM-41	11.3	42.5	23.2	21.3	1.5	11.5	2.82
Ni ₂ P/CeO ₂	5.2	41.3	43.5	10.0	5.2	0.0	1.30
Ni ₂ P/Al ₂ O ₃	6.3	64.1	12.4	19.2	4.4	0.0	7.09

¹HYD/DDS = [HDMDBT+MCHT+DMBCH]/[DMBP]

Figure 3-9. The conversion and selectivity of products over the catalysts prepared

after HDS of 4,6-DMDBT at 325°C and 300 psi of H₂ pressure.

Table 3-8. The conversion and selectivity of products over the catalysts prepared after HDS of 4,6-DMDBT at 350°C and 300 psi H₂ pressure

Catalyst	Conv. (%)	Selectivity (%)					HYD/DD S ¹
		HDMDDB T	DMBP	MCHT	DMBC H	Isomer	
NiMoS/Al ₂ O ₃ (Cr424)	46.7	9.9	35.7	42.8	6.5	5.1	1.66
6%NiO 27%MoO ₃ /MCM-41	42.3	20.6	50.9	4.5	4.7	19.3	0.59
6%CoO 27%MoO ₃ /MCM-41	38.9	22.5	40.6	5.8	6.1	25.0	0.85
6%NiO 27%MoO ₃ -NTA /MCM-41	29.9	22.8	28.2	39.1	2.9	7.0	2.30
6%CoO 27%MoO ₃ -NTA/MCM-41	19.0	20.1	37.8	35.6	2.6	3.9	1.54
3%NiO 14%MoO ₃ /CeO ₂ (Rhoida)	25.2	42.5	13.9	32.9	6.2	4.5	5.88
3%CoO 14%MoO ₃ /CeO ₂ (Rhoida)	22.6	41.7	21.3	22.2	4.3	10.6	3.21
Ni ₂ P/MCM-41	12.5	39.2	39.9	19.1	1.9	0.0	1.51
Ni ₂ P/CeO ₂	4.7	48.4	38.6	7.7	5.3	0.0	1.59
Ni ₂ P/Al ₂ O ₃	7.0	61.2	14.5	19.6	4.7	0.0	5.92

¹HYD/DDS = [HDMDBT+MCHT+DMBCH]/[DMBP]

Figure 3-10. The conversion and selectivity of products over the catalysts prepared after HDS of 4,6-DMDBT at 350°C and 300 psi of H₂ pressure.

3.1.3. Summary

3.1.3.1. Adsorptive desulfurization and denitrogenation

Liquid-phase adsorption of a model fuel containing aromatics, sulfur and nitrogen compounds over different adsorbents were carried out in a fix-bed adsorption system. Different breakthrough curves and selectivity provided an insight into the fundamental understanding of the adsorption mechanism over various adsorbents. Each adsorbent showed very different adsorption properties and capacities (breakthrough and saturate) of aromatic, sulfur and nitrogen compounds.

For the zeolite-based adsorbents, the breakthrough of sulfur compounds was not separated from that of aromatic compounds, but it was clearly separated from the breakthrough of nitrogen compounds of which capacity was higher than those of aromatic and sulfur compounds. The selectivity of indole and quinoline were 5.0 and 7.0, respectively. For the nickel-based adsorbent, the breakthrough capacities of adsorbates were higher than the zeolite-based adsorbent, especially the capacities of sulfur compounds were higher than those of aromatic compounds, but not than those of nitrogen compounds. The selectivity of DBT and DMDBT were 3.1 and 2.0, respectively. It also indicates that the nickel-based adsorbent could be good for selective removal of the sulfur compounds without the steric hindrance from hydrocarbon stream, such as gasoline, kerosene and jet fuel.

The adsorption selectivity on the activated alumina depends on the polarity and the acidic-basic interaction. The activated alumina is very good for selective separation of

nitrogen compounds, especially for basic nitrogen compounds, but not very successful for separating the sulfur compounds from hydrocarbons.

The activated carbon shows higher adsorptive capacity and selectivity for sulfur and nitrogen compounds than other adsorbents used in this study. In the adsorption of sulfur compounds, the activated carbon was good for the sulfur compounds with methyl groups, such as 4,6-DMDBT.

In the adsorption of LCO on the activated carbon, the capacity of sulfur was pretty similar to that in the adsorption of model fuel while that of nitrogen was much lower than that in that of model fuel. It may be because LCO contains and non-basic nitrogen compounds, carbazole-type nitrogen compounds, which has very low reactivity and adsorptivity on catalytic active site. Therefore, the earlier breakthrough of nitrogen results from the non-basic nitrogen compounds to 0.8 of C/C_0 ratio and then basic nitrogen compounds adsorb further on the activated carbon to saturation of nitrogen compounds.

3.1.3.2. Hydrodesulfurization of 4,6-DMDBT

Supported NiMo and CoMo catalysts were prepared with wet co-impregnation, which provided more activity to NiMo and CoMo/MCM-41 catalysts as compared with catalysts prepared with incipient wetness impregnation. It may be because the acidity of MCM-41 support was affected by water solution and preparation method. High metal loaded NiMo/MCM-41 catalyst has higher activity at 300 and 325°C than other catalysts tested in this project and even higher than a commercial NiMo catalyst (Cr424), but which had higher activity at 350°C than NiMo/MCM-41.

Isomerized product of DMDBT was detected on NiMo/MCM-41 at 300°C and most of catalysts at 325 and 350°C except Ni phosphide catalysts. The catalysts which had isomerized product had low HYD/DDS ratio and high DMBP selectivity. 4,6-DMDBT has steric hindrance of two methyl groups at 4- and 6- positions which hinders the direct adsorption of sulfur atom on catalytic active site. If one or two of them move to other positions of DBT, their steric hindrance will disappear or be reduced and sulfur atom may directly adsorb on active site. This results in higher production of DMBP and lower HYD/DDS ratio.

3.1.4. Future work

3.1.4.1 Adsorptive denitrogenation of model feed for deep hydrodesulfurization

Improving the capacity and selectivity of sulfur and nitrogen of activated carbon to other aromatic compounds and contaminant will be performed after investigation of fuel composition of light cycle oil (LCO).

Adsorptive denitrogenation of LCO and RCO will be performed on activated carbon and modified carbon adsorbents at the same adsorption conditions performed in this study and the hydrodesulfurization of the denitrogenated LCO and RCO will also be performed.

3.1.4.2 Development of deep hydrodesulfurization catalysts

New type of catalysts (noble metals, eg.; Pd, Pt and Pd/Pt) with different pretreatment (presulfidation, reduction and etc.) will be performed on hydrodesulfurization and hydrodenitrogenation simultaneously over them with kinetically approaches.

Hydrodesulfurization of LCO and RCO over commercial catalysts and new developed catalysts (NiMo/MCM-41 and supported Pd, Pt, Pd/Pt catalysts) will be performed before/after adsorptive denitrogenation/desulfurization.

Subtask 3.2. Saturation of Two-Ring Aromatics

As a part of the DOE refinery integration project, this sub-task aims at saturating aromatics for high-quality diesel and distillate fuels. High aromatics content in distillate fuels is undesirable since it lowers the fuel quality and contributes to the formation of environmentally harmful emissions. In general, lower aromatics content leads to increased thermal stability, improved combustion characteristics and less soot formation. The conventional method of dearomatization is by aromatics saturation (hydrogenation). Typically, sulfided Co-Mo/Al₂O₃ or Ni-Mo/Al₂O₃ catalysts are employed for hydrogenation. However, these catalysts are most active at higher temperatures where equilibrium limitations may prevent complete hydrogenation. Noble-metal catalysts are active at lower temperatures, where equilibrium limitations can be overcome, however sulfur-tolerance is a major obstacle to their commercial application.

To meet the fuel performance and compositional specifications for diesel fuel, it is necessary for both RCO and LCO to be hydrogenated. This work focuses on the development of increasingly sulfur-tolerant, noble-metal catalysts for the low-temperature hydrotreating and dearomatization (LTHDA) of distillate fuels for the production of ultra-clean and low-aromatic diesel fuels. In this reporting period, the influence of support acidity, preparation method, Pd precursors, support type, bimetallic

Pd-Pt catalyst, etc., on the property of the catalysts were examined. The poisoning effect of different sulfur compounds was clarified.

3.2.1 Experimental

3.2.1.1 Catalyst Preparation

Zeolite supports were obtained from Zeolyst International (formerly PQ Corporation).

All zeolite supports were first calcined in air flow (~60 mL/min) for 4 hours at 450 °C, with a heating rate of approximately 1.5 °C/min, before catalyst preparation. Thus, any supports received in the NH_4^+ form were converted to the H^+ form. Properties of catalyst supports used in this work are summarized in **Table 3-9**.

All catalysts were prepared by the incipient wetness impregnation (IWI) technique. The pore volume of a given support was determined by measuring the volume of water added dropwise to a known weight of the support until the support changed appearance from dry to slightly liquid. The appropriate amount of metal precursor, calculated for the desired metal loading, was dissolved in a total volume of water (and HCl) equal to the pore volume for the support being impregnated.

Table 3-9 Properties of Catalyst Supports, as Received

Support Type	Support Code	SiO₂/Al₂O₃ Ratio	Surface Area (m²/g)	Cation Form
Mordenite	CBV21A	20	500	NH ₄ ⁺
Mordenite	CBV30A	38	512	NH ₄ ⁺
Mordenite	CBV90A	90	500	H ⁺
Y Zeolite	CBV720	30	780	H ⁺
Y Zeolite	CBV780	80	780	H ⁺
ZSM-5	CBV5524G	50	425	NH ₄ ⁺
ZSM-5	CBV8014	80	425	NH ₄ ⁺

All catalysts in this work were prepared with a metal loading of 2 wt%. The precursor metal salt solution was then added dropwise to the support. After a few drops were added, the mixture was stirred thoroughly, then a few more drops were added and the mixture was stirred again. Impregnation continued in this manner until all of the metal solution was loaded on the support. After the impregnation was complete, the catalysts were dried at 110 °C for at least 2 hours. After drying, the catalysts were calcined in air flow (~60 mL/min) at 450 °C for 4 hours, with a heating rate of approximately 1.5 °C/min. The calcined catalysts were then pelletized, crushed and sieved to a particle size of 18-35 U.S.A. Standard Testing Sieve Mesh (0.5 – 1.0 mm).

The metal precursors used in this study were: PdCl₂ (Pressure Chemical), Pd(NO₃)₂·xH₂O (Aldrich, 99.9%) and PtCl₄ (Pressure Chemical). For Pd(NO₃)₂·xH₂O, it was determined from the manufacturer that the degree of hydration is approximately 2. In order to dissolve PdCl₂ in water, it is necessary to add HCl to form soluble PdCl₄²⁻ species. For the first series of catalysts, large amounts of HCl were used – approximately 90% of the pore volume was added as 37 wt% HCl. It was hypothesized that so much HCl might

cause dealumination of the zeolite framework. Also for the first series of catalysts, the supports were not dried prior to impregnation. For all catalysts prepared after the initial series, supports were dried at 110 °C overnight prior to impregnation and HCl was only added in sufficient quantities to dissolve PdCl₂ (< 0.4 mL). It should be noted that for Pt precursors and for Pd(NO₃)₂·xH₂O, it was not necessary to add HCl.

Table 3-10 Catalysts Prepared for this Work

Catalyst	Metal Loading (wt %)	Precursor Metal	Support (SiO ₂ /Al ₂ O ₃ Ratio)	Notes
Pd/CBV21A	2.0	PdCl ₂	Mordenite (20)	
Pd/CBV30A	2.0	PdCl ₂	Mordenite (38)	
Pd/CBV90A	2.0	PdCl ₂	Mordenite (90)	
Pd/CBV720	2.0	PdCl ₂	Y Zeolite (30)	
Pd/CBV780	2.0	PdCl ₂	Y Zeolite (80)	
Pd/CBV5524G	2.0	PdCl ₂	HZSM-5 (50)	
Pd/CBV8014	2.0	PdCl ₂	HZSM-5 (80)	
Pd/Al ₂ O ₃ *	2.0	PdCl ₂	Alumina	
Pd/CBV30A *	2.0	PdCl ₂	Mordenite (38)	
Pd/CBV720 *	2.0	PdCl ₂	Y Zeolite (30)	
Pd/CBV5524G *	2.0	PdCl ₂	HZSM-5 (50)	
Pd/MCM-41(50) *	2.0	PdCl ₂	MCM-41 (50)	
Pt/CBV720 *	2.0	PtCl ₄	Y Zeolite (30)	
Pd-Pt/CBV720 *	2.0	PdCl ₂ , PtCl ₄	Y Zeolite (30)	Pd:Pt = 4:1 mol
Pd/CBV30A ^	2.0	Pd(NO ₃) ₂ ·xH ₂ O	Mordenite (38)	
Pd/CBV720 ^	2.0	Pd(NO ₃) ₂ ·xH ₂ O	Y Zeolite (30)	

A list of catalysts prepared for this work is given in **Table 3-10**. The first series of catalysts, prepared without drying of the support and with large quantities of HCl added, are given no special designation (e.g. Pd/CBV30A). Catalysts prepared with overnight drying of the support prior to impregnation and added HCl sufficient only to dissolve PdCl₂ are denoted with an asterik (e.g. Pd/CBV30A *). Catalysts prepared from

$\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ are denoted with a caret (e.g. Pd/CBV30A^). It should be noted that catalysts prepared from $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ also used supports that were also dried overnight prior to impregnation. Bimetallic catalysts were prepared by co-impregnation of both metal precursors.

3.2.1.2 Catalyst Characterization

BET surface area data was obtained using a Quantachrome Autosorb 1 apparatus. Metal dispersion data was obtained using a Micrometrics 2910 Autochem analyzer. For CO pulse chemisorption, the catalyst was reduced in 5% hydrogen flow in argon (20 mL/min), at atmospheric pressure, under the same temperature ramp as for an experiment (2 °C/min to 225 °C). The sample was outgassed in argon for 10 min, then the temperature was brought down to 50 °C for chemisorption analysis. The sample was dosed with discrete volumes of 10% CO in argon and the uptake was recorded. The doses were repeated until no more CO uptake was detected. The volume of CO adsorbed was used to calculate the percent metal dispersion, assuming a metal:CO stoichiometric ratio of 1:1. For hydrogen chemisorption, the catalyst was reduced in 5% hydrogen flow in argon (20 mL/min), at atmospheric pressure, with a heating rate of 5 °C/min, from ambient to 250 °C. The sample was then degassed in argon for 120 min, then the temperature was brought down to 50 °C for chemisorption analysis. The sample was dosed with discrete volumes of 25% hydrogen in argon and the uptake was recorded. The doses were repeated until no more hydrogen uptake was recorded. The volume of hydrogen adsorbed was used to calculate the percent metal dispersion, assuming a

metal:H₂ ratio of 2:1. The accuracy of metal dispersion data is given by the manufacturer to be +/- 5%.

The Micrometrics 2910 Autochem Analyzer was also used for the temperature-programmed reduction of the catalyst samples. The sample was reduced in 5% hydrogen in argon as the temperature was increased from ambient to 500 °C at 5 °C/min.

Hydrogen uptake is monitored and reveals the temperature at which the catalyst is reduced.

The elemental surface concentrations, metal oxidation states and binding energies of selected catalysts were determined using XPS. A Kratos Analytical Axis Ultra instrument was used. XPS quantification was performed by applying the appropriate instrumental transmission function and elemental relative sensitivity factors (RSFs) for the Kratos instrument to the integrated peak areas. The RSFs are determined taking into consideration the X-ray cross section and relative inelastic mean free paths of the photoelectrons. The approximate sampling depth was 50 Å under these conditions.

3.2.1.3 Catalyst Evaluation in Hydrogenation Experiments

Feedstock composition for hydrogenation experiments was approximately 20 wt% tetralin (Aldrich, 99%), 75 wt% hexadecane (Aldrich, 99+%), and 5 wt% nonane (Aldrich, 99+%), with ppm quantities of sulfur, added as benzothiophene (BT) (Fluka, 99%), dibenzothiophene (DBT) (Aldrich, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT) (Aldrich, 97%) or tetrahydrothiophene (THT) (Aldrich, 99%).

The reaction was carried in a down flow reactor system as described in previous report.

For each experiment, 0.5g of catalyst particles (18-35 mesh) were used. 3.0g of γ -Al₂O₃

particles, also 18-35 mesh, were mixed with the catalyst particles to act as a diluent. Prior to each experiment, catalysts were reduced *in situ*, under a hydrogen flow of 100 mL/min. The pressure was maintained at 100 psi. The temperature was increased from room temperature to 225 °C at a rate of 2 °C/min. The temperature was maintained at 225 °C for two hours prior to the introduction of liquid feed. After the reduction step was complete, the pressure was increased to 600 psi and the hydrogen flow was reduced to 80 mL/min. Liquid feed was then introduced at a rate of 0.08 mL/min. This corresponds to a gas-to-liquid ratio (G/L) of approximately 1000 and a weight hourly space velocity (WHSV) of approximately 8 hr⁻¹. After starting the HPLC pump to introduce liquid feedstock, the system was allowed to equilibrate for 1.5 hr. Therefore, 90 min after the start of feedstock was designated as time-on-stream (TOS) equal to zero. Liquid samples were then collected at 30 min intervals until the experiment was terminated. For the majority of experiments, sulfur-free feedstock was fed until TOS = 2 hr, at which point sulfur-containing feedstock was introduced. Exceptions to this practice were experiments using only sulfur-free feed, and a series of experiments using only sulfur-containing feedstock. The liquid products were analyzed using a Shimadzu GC-17a gas chromatograph coupled with a Shimadzu QP-5000 quadrupole mass spectrometer. The capillary column (30m x 0.25mm, Restek XTI-5) was coated with a 0.25 μ m stationary phase of 5% phenyl-95% methyl polysiloxane.

For selected experiments, the gaseous effluent was analyzed for the presence of hydrogen sulfide (H₂S) using Sensidyne GASTEC detector tubes. The tubes contain lead acetate (Pb(CH₃COO)₂), which reacts with H₂S to form lead sulfide (PbS), changing color from white to reddish-brown. The liquid products from certain other experiments were also

analyzed for sulfur content using an ANTEK 9000 Series Sulfur Analyzer with a lower detection limit of 0.5 wppm sulfur.

3.2.2 Results and Discussions

3.2.2.1 Effect of support acidity

The results of hydrogenation experiments on a series of mordenite catalysts with different acidities (as indicated by their $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios), are shown in **Figures 3-11 and 3-12**.

No clear differences were observed in the conversion or decalin ratio. It might be expected that the more acidic support would exhibit greater sulfur tolerance, due to the imparting of electron deficiency on the Pd metal by the acid sites [3-10], however this was not observed. The effect of support acidity therefore, remains to be determined. Because no discernable differences were observed in catalysts with different support acidities, it was hypothesized that the method of catalyst preparation was potentially flawed. Since large amounts of HCl were used in order to dissolve the PdCl_2 metal precursor, it is possible that dealumination of the zeolite support was occurring. This would render the differences in support acidity negligible.

It was also determined that, just as a matter of good preparation technique, the catalyst supports should be thoroughly dried before impregnation, so the support surface would be free of any water and the true pore volume of the support could be exploited. The effects of this new method of catalyst preparation are examined in the next section.

Figure 3-11 Conversion vs. TOS for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

Figure 3-12 t-DHN/c-DHN ratios for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

3.2.2.2 Effect of Preparation Method

As previously mentioned, the new method of catalyst preparation used about one-tenth the amount of HCl, just enough to dissolve PdCl₂, and the supports were carefully dried overnight prior to impregnation. The characterization properties of catalysts prepared by the old and new methods are presented in **Table 3-11**. Little difference can be seen in BET surface area or dispersion between the two sets of catalysts. Hydrogenation experiments with CBV720 catalysts prepared by the old and new methods, shown in **Figure 3-13**, also show little improvement. The conversion of tetralin and *trans*-/*cis*-decalin ratio was slightly higher for the catalyst prepared by the new method. XPS analysis of the spent Pd/CBV720 and Pd/CBV720* samples revealed that the Pd 3d_{5/2} binding energies were 336.4 and 336.3 eV, respectively. This is an indication that little difference can be discerned in the Pd-support interaction in both catalyst samples.

Table 3-11 Characterization of selected catalysts prepared by the old and new methods

Catalyst	BET Surface Area (m ² /g)	Dispersion (CO)	Dispersion (H ₂)
Pd/Al ₂ O ₃	156	32%	54%
Pd/CBV720	610	34%	39%
Pd/CBV30A	317	35%	41%
Pd/CBV5524G	355	27%	31%
Pd/MCM-41(50)	705	29%	36%
Pd/Al ₂ O ₃ *	165	24%	47%
Pd/CBV720*	590	31%	42%
Pd/CBV30A*	392	35%	47%
Pd/CBV5524G*	328	34%	33%
Pd/MCM-41(50)*	1044	29%	43%

Figure 3-13 Conversion and t-DHN/c-DHN ratio for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 sulfur as BT.

Though the improvement in catalytic properties and hydrogenation activity is only marginal at best, it is nevertheless recommended that the new method of catalyst preparation, with about one-tenth the amount of HCl and careful drying of the support, should be preferred as a matter of good catalyst preparation technique.

3.2.2.3 Effect of Pd Precursor

Two Pd catalysts, Pd/CBV720[^] and Pd/CBV30A[^], were prepared from Pd(NO₃)₂·xH₂O (x ~ 2) to examine the effect of metal precursor on catalytic characteristics and performance. It was hypothesized that, since the Pd(NO₃)₂·xH₂O does not require any HCl to be dissolved in water, catalysts prepared using it as a precursor might exhibit beneficial characteristics compared with those prepared from PdCl₂, which requires

addition of HCl. However, this was not observed to be the case. **Figure 3-14** and **Figure 3-15** show that the catalysts prepared from nitrate precursors significantly underperformed their chloride counterparts.

The properties of the catalysts from nitrate precursors and those of their chloride counterparts, are shown in **Table 3-12**. The most glaring difference between the catalysts prepared from nitrate precursors is their poor dispersion. It is unclear why catalysts prepared from $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ would be so poorly dispersed. It should be mentioned that, upon obtaining such poor results with the first set of catalysts prepared from $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, both Pd/CBV720[^] and Pd/CBV30A[^] were prepared and characterized a second time and both catalysts had similarly poor dispersions, as measured by CO pulse chemisorption (7% and 8%, respectively).

Table 3-12 Properties of catalysts from nitrate and chloride precursors

Catalyst	BET Surface Area (m ² /g)	Dispersion (CO)	Dispersion (H ₂)
Pd/CBV720*	590	31%	42%
Pd/CBV720 [^]	747	8%	7%
Pd/CBV30A*	392	35%	47%
Pd/CBV30A [^]	412	8%	10%

XPS analysis of the spent Pd/CBV720* and Pd/CBV720[^] catalyst samples revealed Pd 3d_{5/2} binding energies of 336.4 and 335.7 eV, respectively. The higher binding energy of the Pd/CBV720* catalyst sample indicates a stronger metal-support interaction, representative of smaller and more electron-deficient metal particles [3-11]. This is consistent with the hydrogen pulse chemisorption data, from which the average metal

particle diameters were calculated to be 2.6 nm for Pd/CBV720* and 15.3 nm for Pd/CBV720[^].

Figure 3-14 Conversion vs. TOS for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

Figure 3-15 t-DHN/c-DHN ratio for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

It can be concluded that catalysts prepared from PdCl₂, under the conditions for catalyst preparation used in this study, are superior to catalysts prepared from Pd(NO₃)₂·xH₂O, both in terms of catalyst characteristics and sulfur tolerance during the hydrogenation of tetralin in the presence of sulfur, under the reaction conditions used in this study.

3.2.2.4 Effect of Support Type

The effect of support type was re-examined with catalysts prepared by the new method. The results are presented in **Figure 3-16** and **Figure 3-17**. Not surprisingly, the catalytic performance is very similar to the catalysts prepared by the old method. The Y-zeolite-supported (CBV720*) catalyst exhibited the greatest sulfur tolerance of the catalysts tested. As before, there is no clear trend between catalytic performance and BET surface area or metal dispersion. It is again obvious, therefore, that support structure has a significant impact on the sulfur tolerance of Pd catalysts.

Considering that the average particle diameters, shown in **Table 3-13**, are larger than the zeolite pore openings, it is likely that the majority of metal particles do not reside in the zeolite pore structure, but rather on the zeolite exterior surface. It is therefore difficult to speculate why one support would intrinsically perform better than another.

Table 3-13 Properties of Selected Catalysts

Catalyst	Dispersion (H ₂)	Active Particle Diameter (nm)	Zeolite Pore Size (Å)
Pd/Al ₂ O ₃ *	47%	2.3	-
Pd/CBV720*	42%	2.6	7.4
Pd/CBV30A*	47%	2.4	6.7 x 7.0
Pd/CBV5524G*	33%	3.5	5.3 x 5.6
Pd/MCM-41(50)*	43%	2.6	15 – 100

Figure 3-16 Conversion vs. TOS for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

Figure 3-17 t-DHN/c-DHN ratio for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

Figure 3-18 Conversion vs. TOS for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressures in the presence of 100 ppm sulfur as BT.

Figure 3-19 t-DHN/c-DHN ratio for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as BT.

3.2.2.5 Bimetallic Pd-Pt Catalyst

The addition of Pt to Pd catalysts has been reported to increase the hydrogenation activity and improve resistance to poisoning by sulfur. Specifically [3-12, 3-13], it has been shown that optimum content of Pd and Pt is found at a mole ratio of 4 Pd to 1 Pt.

Therefore, a Pd-Pt(4:1)/CBV720* catalyst was synthesized and compared to Pd/CBV720* and Pt/CBV720*. The results are presented in **Figure 3-18** and **Figure 3-19**.

The Pd-Pt/CBV720* catalyst maintained 100% tetralin conversion even after both Pd/CBV720* and Pt/CBV720* catalysts began to show deactivation due to sulfur poisoning. Additionally, the *trans*-/*cis*-decalin ratio was maintained at a higher level. This indicates that the bimetallic combination did, in fact, provide an enhancement in sulfur tolerance, as compared with the monometallic catalysts. The characterization of the Pd, Pt and Pd-Pt catalysts is presented in **Table 3-14**.

Table 3-14 Characterization of Pd, Pt and Pd-Pt catalysts supported on CBV720*

Catalyst	BET Surface Area (m ² /g)	Dispersion (CO)	Dispersion (H ₂)
Pd/CBV720*	590	31%	42%
Pt/CBV720*	618	60%	63%
Pd-Pt/CBV720*	623	42%	52%

The dispersion of the Pt/CBV720* catalyst is exceptionally high, which may explain why it performed slightly better than Pd/CBV720*. However, dispersion alone cannot be responsible for increased sulfur tolerance, as the bimetallic Pd-Pt catalyst outperformed the Pt catalyst, despite having a lower dispersion. It is noted [3-12] that Pd and Pt form an alloy at structure at Pd:Pt = 4:1. The high sulfur tolerance of Pd-Pt (4:1)/USY(680)

catalyst was attributed to “structural and electronic effects rather than to the degree of metal dispersion” [3-12]. Furthermore, EXAFS analysis of a Pd-Pt (4:1)/SiO₂-Al₂O₃ catalyst revealed a chemical bond between Pd and Pt, and the high hydrogenation activity of the catalyst was attributed to this direct interaction [3-13].

Binding energies from XPS analysis of spent catalyst samples are shown in **Table 3-15**.

The increase in the binding energy for both the Pd 3d_{5/2} and Pt 4f_{7/2} in the bimetallic catalyst indicates a greater metal-support interaction compared with the individual monometallic catalysts.

Table 3-15 Binding Energies from XPS analysis for Pd, Pt and Pd-Pt catalysts

Spent Catalyst Sample	Pd 3d _{5/2} Binding Energy (eV)	Pt 4f _{7/2} Binding Energy (eV)
Pd/CBV720*	336.4	-
Pt/CBV720*	-	72.2
Pd-Pt/CBV720*	336.7	72.3

3.2.2.6 Poisoning Effects of Different Sulfur Compounds

The hydrogenation of tetralin was tested on Pd/CBV30A* catalyst with 100 ppm sulfur feedstock using DBT, 4,6-DMDBT and THT, in addition to BT, in order to examine the effect of the type of sulfur species on sulfur poisoning of hydrogenation catalysts. The conversion results of the hydrogenation experiments are presented in **Figure 3-20**. The results with BT, DBT and 4,6-DMDBT are remarkably similar.

Figure 3-20 Conversion vs. TOS for the hydrogenation of tetralin over Pd/CBV30A* catalyst at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as different sulfur compounds.

Figure 3-21 t-DHN/c-DHN ratio vs. TOS for the hydrogenation of tetralin over Pd/CBV30A* catalyst at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as different sulfur compounds.

The Pd/CBV30A* catalyst exhibited almost identical deactivation with these three sulfur compounds. The deactivation was somewhat accelerated and final tetralin conversion was somewhat lower when THT was the sulfur compound in the feed. One possible explanation of this behavior may be the electron density on the sulfur atom of the particular sulfur compound, shown in **Table 3-16 [3-14]**. The electron densities on the sulfur atoms in BT, DBT and 4,6-DMDBT are very similar, however for THT, the electron density is much greater. The higher electron density may result in a stronger interaction with the Pd particles, resulting in a greater poisoning effect.

The *trans*-/*cis*-decalin ratios are shown in **Figure 3-21**. The *trans*-/*cis*-decalin ratio appears to be unaffected by the species of sulfur present in the feedstock.

Table 3-16 Electron Density on the Sulfur Atom for Selected Sulfur Compounds [3-14]

Sulfur Compound	Electron Density on Sulfur Atom
Benzothiophene (BT)	5.739
Dibenzothiophene (DBT)	5.758
4,6-dimethyldibenzothiophene (4,6-DMDBT)	5.760
Tetrahydrothiophene (THT)	6.042

In order to attempt to determine the fate of sulfur compounds during the hydrogenation experiments, several analyses were performed. There are three possible scenarios for the sulfur species in the feedstock; 1) The sulfur compounds have a weak interaction with the catalyst and pass through the reactor without undergoing reaction, 2) The sulfur compounds adsorb on the catalyst and remain there unreacted, or 3) The sulfur compounds are adsorbed on the catalyst and undergo reaction.

In experiments with each sulfur compound, the gaseous effluent of the reactor was analyzed for the presence of hydrogen sulfide. In all cases, H₂S was detected, and the

concentration of H_2S present in the product gasses increased with TOS. Therefore, at least some of the sulfur species present in the feedstock are undergoing hydrodesulfurization reactions to form H_2S .

The outlet sulfur concentrations of the liquid products from the hydrogenation of tetralin over Pd/CBV30A* were analyzed. These results are shown in **Figure 3-22**.

Even after 11 hours TOS, the sulfur concentration of the products is below 10 ppm (except in the case of 4,6-DMDBT). Since the inlet sulfur concentration is 100 ppm, the majority of the sulfur is either converted to H_2S or retained on the catalyst. It is interesting that the outlet sulfur concentration plot resembles breakthrough curves for sulfur compounds on adsorbents for sulfur removal of liquid fuels, e.g. [3-15, 3-16, 3-17]. Indeed, 4,6-DMDBT is most difficult to remove from liquid fuels due to the steric hindrance of the methyl groups in the 4 and 6 positions, which shield the sulfur atom.

Figure 3-22 Outlet sulfur concentration vs TOS for the hydrogenation of tetralin over Pd/CBV30A* catalyst at 225 °C and 600 psig hydrogen pressure in the presence of 100 ppm sulfur as various sulfur compounds.

It is not surprising, therefore, that as the reaction proceeds and perhaps the surface coverage of sulfur is very high, that the order of final outlet sulfur concentration proceeds in the order of steric hindrance to sulfur adsorption: 4,6-DMDBT > DBT ~ BT > THT.

Since most of the THT is retained, this might also explain the fact that tetralin conversion is inhibited to a larger extent when THT is the sulfur compound in the feed.

The XPS analysis of spent catalyst samples from several experiments was unable to detect any sulfur and provide any information regarding the presence of sulfur on the spent catalyst or the nature of any sulfur on the catalyst. It is possible that the sulfur on the catalyst was removed by the flushing of the reactor with hexadecane after the experiments, or more likely, by the hexane wash prior to XPS analysis. Alternatively, it is also possible that the sulfur is present in a concentration too low to be detected by XPS. Previously [3-18], it has been shown that Pd catalysts that have experienced deactivation due to sulfur will completely regain tetralin hydrogenation activity after the feedstock is switched to one which contains no sulfur. The reversibility of Pd hydrogenation catalysts was also demonstrated by [3-19] with *in-situ* removal of H₂S using ZnO in batch reactions. It is therefore likely that any sulfur species adsorbed on the catalyst is undergoing hydrodesulfurization reactions to form H₂S, rather than remaining on the Pd particle as a metal-sulfide.

Conclusions

Based on experiments on various catalysts for the hydrogenation of tetralin at 225 °C and 600 psig hydrogen pressure, in the presence of sulfur, and also on the characterization of the catalysts prepared for this study, the following conclusions can be derived:

Y-zeolite supported catalysts were shown to exhibit higher sulfur tolerance than any of the other supports tested, under the reaction conditions and methods of catalyst preparation employed in this study.

The effect of support acidity remains to be determined. A series of mordenite catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (20, 38 and 90) was tested and no discernable differences were observed in activity for tetralin hydrogenation. Catalysts prepared from the metal precursor $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ have very poor metal dispersion and significantly underperform catalysts synthesized from PdCl_2 in the hydrogenation of tetralin. The addition of Pt to Pd, in the mole ratio of 4 Pd:1 Pt, exhibits greater sulfur tolerance than Pd or Pt catalysts alone.

The *trans*-/*cis*-decalin ratio was unaffected by the type of sulfur compound present in the feedstock, among BT, DBT, 4,6-DMDBT and THT.

The conversion of tetralin was largely unaffected by the type of sulfur compound among BT, DBT and 4,6-DMDBT, however THT has a greater poisoning affect than the others. This may be due to the high electron density of the sulfur atom in THT, which could potentially produce a greater sulfur-palladium interaction.

The majority of sulfur in the feedstock undergoes hydrodesulfurization reactions to form H_2S .

Subtask 3.3. Value-Added Chemicals from Naphthalene and Biphenyl

In previous year, the methylation of 2-methylnaphthalene (2-MN) with methanol by using zeolitic catalysts were investigated. Iron modified ZSM-5 zeolite (Fe-MFI molecular sieve) catalyst showed a high 2-MN conversion, 2,6-dimethylnaphthalene (2,6-DMN) yield and 2,6-DMN/2,7-DMN selectivity. In this year, we intend to further explore new catalyst formulation with improved catalyst performance and to identify the active species of transition metal in the selected catalyst. In this report period, Fe-MFI catalysts have been characterized by elemental analysis, XRD, TEM, and DMN adsorption experiment. The effect of sulfur compounds in the 2-MN feed stock on the performance of catalyst was examined. In addition to the methylation of 2-MN, selective methylation of 4-methylbiphenyl (4-MBP) to 4,4'-dimethylbiphenyl (4,4'-DMBP) was briefly investigated.

3.3.1. Experimental

3.3.1.1 Catalysts

HZSM-5 (Supplied by Zeolyst International) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50 (CBV5524G), 80 (CBV8014) and 280 (CBV28014) were used as catalyst. For methylation of 2-MN, iron-modified ZSM-5 were tested as catalyst. Iron-modified ZSM-5 catalysts were prepared by modifying the HZSM-5 with iron fluoride ($\text{FeF}_3 \cdot 3\text{H}_2\text{O}$) and ammonium hydrogen fluoride (NH_4HF_2) at elevated temperature. The detailed process was described in the previous reports. For methylation of 4-MBP, the catalysts were prepared by modifying the HZSM-5 with 15% NH_4F . In a typical process, 5 g HZSM-5 was mixed

with 50 ml 15% NH_4F solution with stirring overnight at room temperature. Then, the mixture was dried at 100 °C and calcined at 450 °C for 5 h.

3.3.1.2 Catalyst Characterization

X-ray powder diffraction (XRD) was done on a Scintag 3100 diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation. Samples were mixed with ca. 10 wt% 325 mesh silicon internal standard for 2θ correction. Jada Program was used to calculate the lattice constants.

Imaging of the samples was obtained through high resolution transmission electron microscopy (HR-TEM). For this purpose, a Philips 420 electron microscope was used and operated at 120 kV. Samples were positioned on a carbon microgrid, supported on copper, by placing a few droplets of a suspension of ground sample in ethanol. The grid was dried at ambient conditions.

Composition of the catalysts was analyzed by a Leeman Labs PS3000UV ICP (inductively coupled plasma emission spectrophotometer).

Selective adsorption of DMNs was carried out in a batch system. 1 g catalyst was mixed with 10 ml 10 wt% DMNs isomer mixture under stirring for 24 h at room temperature, after which the suspension was centrifugalized and the solution was analyzed. The adsorbed amount was calculated based on the mass balance before and after adsorption.

3.3.1.3 Catalyst Evaluation

Catalytic testing was carried out in a down-flow fixed bed reactor system. In a typical run, 0.3 gram catalyst (10-18 mesh) loaded in reactor tube (Pyrex, I.D.: $\frac{1}{2}$ inch) was placed in the furnace center. The catalyst was activated at 450 °C for 1 h under the inert

N₂ gas flow (20 ml/min). Then the temperature was cooled down to the reaction temperature. Reactant dissolved in mesitylene solvent (2-MN:methanol:mesitylene=1:5:5 mol ratio or 4-Methylbiphenyl (4-MBP):methanol:mesitylene=1:5:5) was fed into reactor through a HPLC pump at the flow rate of 1.98 ml/min together with 20 ml/min carrier N₂ gas flow. The reaction product was collected at 1 hour interval. Both the reactants and products were analyzed by HP 5890 gas chromatography (GC) with a β -Dex 120 capillary column (60m, 0.25 mm I.D. column with 0.25 micrometer coating film thickness). Two 2-MN feed stocks, which is purchased from Aldrich and Acros Organics, respectively, were tested for the methylation of 2-MN. 2-MN from Aldrich has a high sulfur concentration of about 5000 ppm and 2-MN from Acros Organics has a low sulfur concentration of 29 ppm.

3.3.2 Results and Discussions

3.3.2.1 Methylation of 2-MN with methanol

3.3.2.1.1 Characterization of Fe-MFI catalysts

HZSM-5 and iron modified HZSM-5 catalysts, which were tested in the previous year, were characterized by XRD and their unit cell dimension were calculated. The results are listed in **Table 3-14**. These results revealed that the a axis expanded after the HZSM-5 zeolite was modified with iron. The a-axis is the zigzag channel of the HZSM-5, which will have significant effect on the shape selective properties of the catalysts. However, the degree of a-axis expansion is different for different modification methods. With the same Fe loading, the wet chemistry iron modification method (M-Fe-06) resulted the biggest expansion on a-axis. The a-axis did not change for Fe-MFI catalyst

prepared by physical mixing method. The more the Fe loadings, the bigger the a-axis expansion. Interestingly, the a-axis dimension also increased when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of HZSM-5 increases, which indicate that Fe may substitute the Al position in the ZSM-5.

Element analysis results of the HZSM-5 or iron modified HZSM-5 was listed in **Table 3-15**. After the wet chemistry iron modification, Al_2O_3 content decreased and Fe_2O_3 content increased (M-Fe-06), while the Al_2O_3 content did not change for ion-exchange (M-Fe-16) or physical mixture method (M-Fe-11). These results indicated that iron was isomorphous substituted the Al position in the framework of HZSM-5 after wet chemistry iron modification. Therefore, the a-axis expansion after the wet chemistry iron modification can also be ascribed to the iron isomorphous substitution of the Al position in the framework of HZSM-5. For Fe-MFI catalyst prepared by physical mixing method, since iron did not enter the framework of HZSM-5, the a axis did not expand after modification.

Two samples, i.e., Fe isomorphous substituted HZSM-5 (M-Fe-06) and Fe ion-exchanged HZSM-5 (M-Fe-16), which have similar Fe contents, were selected for high-resolution transmission electron micrographs measurement. The photographs were shown in **Figure 3-23**. Although the two samples have the similar Fe content, their TEM micrographs are essentially different. For Fe isomorphous substituted HZSM-5, no significant presence of large Fe-containing clusters was observed in most area, although there is Fe-containing cluster in some small area. On the contrary, Fe ion-exchanged HZSM-5 shows big Fe-containing particles on the external surface of the HZSM-5 crystals. These observations indicate that ion dispersion was better in M-Fe-06 than in M-

Fe-16. The better iron dispersion of M-Fe-06 than M-Fe-16 may also be one the reasons for the better catalytic performance (in terms of activity, selectivity and stability) of M-Fe-06 than that of M-Fe-16.

The HZSM-5 and Fe-MFI catalysts were further characterized by DMNs selective adsorption experiment. The results are listed in **Table 3-16**. The HZSM-5 only adsorb 2,7 and 2,3 or 1,4 DMNs. After the HZSM-5 modified with iron, the Fe-MFI can adsorb all the DMN isomers, which may attribute to the expansion of axis of HZSM-5. The change of the adsorption properties of HZSM-5 after modification may co-relate with the change of catalytic properties of HZSM-5 after modification for the selective methylation of 2-MN to 2,6-DMN. However, detailed characterization of the catalysts should be carried out before make a conclusion.

Table 3-17 Lattice constants determined from XRD for HZSM-5 or iron modified HZSM-5

Sample Name	Description	a	b	c
CBV5524G	HZSM-5 SiO ₂ /Al ₂ O ₃ =50	20.0065	19.9362	13.3781
M-Fe-05	Fe/Al=0.16	19.9992	19.9367	13.3631
M-Fe-06	Fe/Al=0.5	20.0587	19.9368	13.3888
M-Fe-07	Fe/Al=1.35	20.0818	19.9521	13.3775
M-Fe-08	Fe/Al=1.75	20.0973	19.938	13.3798
M-Fe-09	Fe/Al=7.0	20.1162	19.9331	13.38
M-Fe-10	Fe/Al=25	20.0711	19.9113	13.3673
M-Fe-11	Fe/Al=0.5, Physical Mix	19.9996	19.965	13.3699
M-Fe-12	Fe/Al=0.5, Fe(NO ₃) ₃	20.0777	19.9587	13.3906
M-Fe-13	Fe/Al=0.5, FeCl ₃	20.0499	19.9816	13.3828
M-Fe-14	Fe/Al=0.5, NH ₄ F	20.085	20.0806	13.393
M-Fe-15	Fe/Al=0.5, FeF ₃ only	20.0421	19.9455	13.3678
M-Fe-16	Ion-exchange	20.0395	19.9491	13.3867
CBV8014	HZSM-5 SiO ₂ /Al ₂ O ₃ =80	20.034	20.0577	13.3769
CBV28014	HZSM-5 SiO ₂ /Al ₂ O ₃ =280	20.0701	20.0284	13.3554
M-Fe-02	CBV28014, Fe/Al=0.5	20.0708	19.9608	13.3683
M-Fe-03	CBV8014, Fe/Al=0.5	20.0609	19.9444	13.3618
M-Fe-04	CBV8014, Fe/Al=5	20.0733	20.0158	13.3502
M-D-Al-01	CBV5524G, NH ₄ HF ₂ only	20.0411	19.9638	13.3734

Table 3-18 Element analysis of HZSM-5 and iron modified HZSM-5

Sample Name	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Na ₂ O (%)	SiO ₂ (%)	LOI (900C)	SiO ₂ /Al ₂ O ₃ (Mol)	Fe ₂ O ₃ /Al ₂ O ₃ (Mol)
CBV5524G	3.06	0.06	<.05	92	4.23	51.11	0.01
M-D-Al-01	2.44	0.08	<.05	92	4.10	64.10	0.02
M-Fe-05	2.56	0.59	<.05	92	3.80	61.09	0.15
M-Fe-06	2.23	1.01	<.05	91	4.11	69.37	0.29
M-Fe-07	1.81	2.31	<.05	93	2.56	87.35	0.82
M-Fe-08	1.73	3.35	<.05	92	3.35	90.40	1.24
M-Fe-09	1.22	9.41	<.05	86	2.31	119.84	4.93
M-Fe-10	0.90	20.8	<.05	74	1.89	139.78	14.76
M-Fe-11	2.99	1.35	<.05	88	6.21	50.03	0.29
M-Fe-14	2.25	1.21	<.05	91	5.05	68.76	0.34
M-Fe-15	2.41	1.15	<.05	90	4.92	63.49	0.30
M-Fe-16	2.76	1.15	<.05	87	5.52	53.59	0.27

Table 3-19 Selective adsorption of DMNs by HZSM-5 and Fe-MFI catalysts

Adsorption Capacity (mg/g)	2,6-DM N	2,7-DM N	1,7-DM N	1,3-DM N	1,6-DM N	(2,3+1,4)-DMN	1,5-DM N	1,2-DM N	1,8-DM N
Feed DMN (wt%)	0.96	0.95	1.14		1.85		0.31	0.09	0.01
	8	6	8	1.12	9	2.016	8	6	9
HZSM-5	0	1.87	0	0	0	2.32	0	0	0
M-Fe-06	4.78	9.89	4.64	5.11	9.4	18.97	1.46	0.43	0.05

Figure 3-23 TEM micrographs of (a) M-Fe-06, and (b) M-Fe-16

3.3.2.1.2 Effect of sulfur compounds on the methylation of 2-MN

During this period, we change the feedstock of 2-MN. Accidentally, we found that the catalytic properties for the same catalyst were significantly different with different 2-MN feedstock. Therefore, the sulfur and nitrogen concentration of 2-MN were analyzed. While the nitrogen compounds concentration were the same, the sulfur compound concentration was significantly different for 2-MN from different company. The 2-MN from Aldrich, which was used in previous year, has a sulfur concentration about 5000 ppm, and 2-MN from Acros Organics has a sulfur concentration of 29 ppm. The significant difference on the reaction results between the two 2-MN feedstocks may be ascribed to the different sulfur concentrations. **Figures 3-24** compares the reaction results of Fe-ZSM-5 catalyst for 2-MN with different sulfur concentrations. The conversion of 2-MN with low sulfur content is higher than that with high sulfur content. Also, the deactivation of the catalyst was slow when low sulfur 2-MN was used. The DMN yield, 2,6-DMN/2,7-DMN ratio and 2,6-DMN/DMNs ratio was also improved

when low sulfur content 2-MN was used as feed stock. While the catalyst was poisoned by the sulfur compound and the 2,6-DMN/2,7-DMN ratio and 2,6-DMN/DMNs ratio decreased with reaction time for 2-MN with high sulfur concentration, the 2,6-DMN/2,7-DMN ratio and 2,6-DMN/DMNs ratio increased with reaction time for 2-MN with low sulfur compound. The improvement on the catalytic performance for HZSM-5 (CBV8014, $\text{SiO}_2/\text{Al}_2\text{O}_3=80$) was more significant than Fe-MFI catalyst. **Figure 3-25** compares the reaction results of HZSM-5 catalyst for 2-MN with different sulfur concentrations. When the sulfur concentration is low, the DMN yield was 10.6 mol%, which is twice that for Fe-MFI catalyst. However, since the low sulfur content 2-MN has 29 ppm sulfur compound, the sulfur still poison the catalyst. Fortunately, a PSU-SARS process, which can removed the sulfur compound to 0.1 ppm, has been developed in our lab. In the next half year, we will combine the PSU-SARS process and methylation of 2-MN reaction together. The sulfur compound in 2-MN will removed through PSU-SARS process before 2-MN methylation reaction. With such low sulfur content, the catalyst is expected to be stable over long period reaction time.

(A)

(B)

(C)

(D)

Figure 3-24 Comparison of the methylation of 2-MN with methanol over Fe-MFI (M-Fe-06) catalyst for 2-MN with different sulfur contents. Reaction conditions: temperature: 300 °C; Feed (2-MN:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min

(A)

(B)

(C)

(D)

Figure 3-25 Comparison of the methylation of 2-MN with methanol over HZSM-5 (CBV8014) catalyst for 2-MN with different sulfur contents. Reaction conditions: temperature: 300 °C; Feed (2-MN:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min.

Methylation of 4-MBP with methanol

3.3.2.2.1 Effect of reaction temperature

Effect of reaction temperature on the methylation of 4-MBP with methanol over NH_4F modified HZSM-5 (CBV8014) was investigated and the results are shown in **Figure 3-26**. The conversion of 4-MBP increased with temperature first, then leveled when the temperature was above 380 °C. The yield of Dimethylbiphenyls (DMBPs), 4,4'-DMBP/DMBPs ratio and 4,4'-DMBP/3,4'-DMBP ratio showed a maximum at temperature between 360-380 °C. Therefore, 380 °C was selected as the reaction temperature for the methylation of 4-MBP in this study.

Figure 3-26 Effect of reaction temperature on the methylation of 2-MBP with methanol over NH_4F modified HZSM-5 (CBV8014). Reaction conditions: Feed (2-MBP:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min.

3.3.2.2.2 Effect of NH_4F modification

Methylation of 4-MBP with methanol over HZSM-5 (CBV8014) with and without NH_4F modification was carried out and the results are shown in **Figure 3-27**. After NH_4F modification, the activity of the catalyst decreased and the conversion of 4-MBP sharply decreased from 60.3% to 12.08%. The decrease in the 4-MBP conversion was mainly caused by the inhibition of 4-MBP isomerization. The yield of DMBPs only slightly decreased from 8.89% to 7.96%. The percentage of desired product 4,4'-DMBP in the DMBPs significantly increased after HZSM-5 modified with NH_4F . Also, the formation of main competitor 3,4'-DMBP was inhibited. The 4,4'-DMBP/3,4'-DMBP ratio increased from 0.29 for HZSM-5 to 5.32 for NH_4F modified HZSM-5. The high 4,4'-DMBP/3,4'-DMBP ratio will significantly reduce the separation cost.

Figure 3-27 Comparison of the methylation of 4-MBP with methanol over HZSM-5 (CBV8014) catalysts with and without NH_4F modification. Reaction conditions: Temperature: 380 °C; Feed (4-MBP:methanol:mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min.

3.3.2.2.3 Effect of SiO₂/Al₂O₃ ratio of HZSM-5

HZSM-5 with different SiO₂/Al₂O₃ ratio were modified by NH₄F and their catalytic performance on the methylation of 4-MBP with methanol are shown in **Figure 3-28**. The catalytic performance of HZSM-5 with SiO₂/Al₂O₃ ratio of 50 and 80 did not have significant difference. However, for HZSM-5 with SiO₂/Al₂O₃ ratio of 280, the catalytic performance was different from that for HZSM-5 with SiO₂/Al₂O₃ ratio of 50 or 80. While the conversion of 4-MBP and yield of DMBPs decreased, the 4,4'-DMBP/DMBPs and 4,4'-DMBP/3,4'-DMBP ratios all increased.

Figure 3-28 Effect of SiO₂/Al₂O₃ ratio of NH₄F modified HZSM-5 on the methylation of 4-MBP with methanol. Reaction conditions: temperature: 380 °C; Feed (2-MBP:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min.

3.3.2.2.4 Effect of Iron modification of HZSM-5

Iron modified HZSM-5 (CBV5524G) has been shown superior catalytic performance on the selective methylation of 2-MN with methanol to 2,6-DMN.

Therefore, M-Fe-06 was tested for the methylation of 4-MBP with methanol and the results are shown in **Figure 3-29**. After iron modification, the conversion of 4-MBP decreased, and the yield of DMBPs, the 4,4'-DMBP/DMBPs and 4,4'-DMBP/3,4'-DMBP ratio all increased. However, although the yield of DMBPs for M-Fe-06 is higher than that for NH₄F modified HZSM-5, 4,4'-DMBP/DMBPs and 4,4'-DMBP/3,4'-DMBP ratios are all much lower than those for NH₄F modified HZSM-5.

Figure 3-29 Methylation of 4-MBP with methanol over HZSM-5 (CBV5524G) and iron modified HZSM-5 (M-Fe-06) catalysts. Reaction conditions: temperature: 380 °C; Feed (2-MBP:methanol: mesitylene=1:5:5 mol ratio): 1.98 ml/hr; Catalyst: 0.3 gram; Gas flow: 20 ml/min.

3.3.3 Summary

After wet chemistry iron modification, iron isomorphously substitutes the Al in HZSM-5. XRD characterization shows that the a axis of MFI zeolite expand after iron modification.

As a results, the iron modified HZSM-5 catalyst can adsorb all the DMN isomers. Before modification, HZSM-5 only adsorb 2,7-DMN and 2,3-DMN or 1,5-DMN.

Sulfur compound has significant poisoning effect on the methylation of 2-MN with methanol over HZSM-5 types zeolite catalyst. When a high sulfur content 2-MN is used as reactant, 2-MN conversion, DMN yield and 2,6-DMN/2,7-DMN ratio all decreases.

The methylation of 4-MBP with methanol over HZSM-5 zeolite prefers to be at 360-380 °C. NH_4F modification significantly improves the catalytic performance of HZSM-5.

High DMBPs yield, 4,4'-DMBP/DMBPs ration and 4,4'-DMBP/3,4'-DMBP selectivity are obtained. The best $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of HZSM-5 for methylation of 4-MBP is 50 or 80. When the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is too high, the conversion of 4-MBP and yield of DMBPs decreased, although the 4,4'-DMBP/DMBPs and 4,4'-DMBP/3,4'-DMBP ratio all increased. Iron modification dose not show superior catalytic performance for methylation of 4-MBP as that for methylation of 2-MN.

3.3.4 Future work

Future work will focus on the continuous development of high quality catalyst and clarifying the relationship among acid property (strength, site, etc), transition metal species, pore structure and catalyst performance (activity and selectivity). The catalysts will be characterized by acidity measurement, XPS, SEM, FT-IR, TPR, TPD, NMR and selective adsorption separation. The effect of sulfur compounds on the methylation of 2-MN will be investigated. PSU-SARS process will be used to remove sulfur compound from 2-MN and the extremely low sulfur 2-MN will be tested for the methylation of 2-MN.

Task 4. Evaluation of Coal-Based Fuel Products

(Prepared by Sharon Falcone Miller, Ronald T. Wincek, and Bruce G. Miller)

The objective of the Task 4 activities is to evaluate the effect of introducing coal into an existing petroleum refinery on the fuel oil product. To accomplish this, the combustion performance and trace element emissions of a fuel oil produced during co-processing were measured in Penn State's watertube research boiler. The combustion performance and trace element emissions for the fuel oil produced by further refining of the light cycle oil-refined chemical oil blend with that from a commercial/petroleum-based No. 6 fuel oil were compared. The testing was performed to determine if differences in the combustion behavior or emissions of the two fuel oils would result from variations in the API gravity, viscosity, or changes in composition including trace elements present in either fuel oil.

Subtask 4.1. Fuel Oil Analysis

The co-processed fuel oil used in the combustion and emissions tests was analyzed by a series of ASTM procedures and the results are shown in **Table 4-1**. **Table 4-1** also contains the analysis of the No. 6 fuel oil used to generate the baseline data previously reported [4-1] and used to stabilize the boiler prior to firing the co-processed fuel oil, which was tested during this reporting period. Analyses were selected that could be used to compare the co-processed fuel oil with a petroleum-based commercial fuel oil. Specifically, they are used to: 1) ensure that the samples meet standardized fuel oil specifications [4-2]; 2) determine the quantity of trace elements in the co-processed fuel oil; and 3) classify the co-processed fuel oil per established specifications [4-2].

The co-processed fuel oil exhibited properties that were characteristic of different grades of fuel oils. For example, the density, both relative and API, were similar to No. 6 fuel oil but started to approach those characteristic of No. 5 fuel oil [4-2]. This was also true of the heating value, which was midway between typical heating values of No. 6 fuel oil (*i.e.*, 150,000 Btu/gal) and No. 5 fuel oil (*i.e.*, 148,900 Btu/gal). Viscosity was noticeably less for the co-processed fuel oil when compared to the No. 6 fuel oil. Viscosity at 100°F was similar to that of No. 5 fuel oil while the viscosity at 130°F was

similar to that of No. 4 fuel oil. The two properties that exhibited the greatest deviation from a No. 6 fuel oil sample were ash and sulfur content. The sulfur content of the co-processed fuel oil was 0.02%, which is less than that typically reported in No. 1 fuel oil (*i.e.*, kerosene) and No. 2 fuel oil (home heating fuel). The ash content of <0.2% is typical of fuel oil grades No. 1, 2, and 4.

Table 4-1. Analysis of No. 6 Fuel Oil and Co-Processed Fuel Oil

Characteristic	Method	No. 6 Fuel Oil	Co-Processed Fuel Oil
Relative Density, 60/60°F	ASTM D 1298-97 e2	0.975 g/ml	0.972 g/ml
Relative Density, 60/60°F, API	ASTM D 1298-97 e2	13.6° API	14.1° API
Viscosity, 100°F	ASTM D 445-03	3,195 ssu	165 ssu
Viscosity, 130°F	ASTM D 445-03	990 ssu	46 ssu
Viscosity, 210°F	ASTM D 445-03	138 ssu	NP ^a
Total Sulfur	ASTM D 4239-04a	0.93% (wt/wt)	0.02% (wt/wt)
Water	ASTM D 1796-97 (2002)	0% (vol/vol)	0% (vol/vol)
Sediment	ASTM D 1796-97 (2002)	0% (vol/vol)	0% (vol/vol)
Ash	ASTM D 482-03	0.06% (wt/wt)	<0.02% (wt/wt)
Higher Heating Value	ASTM D 240-02	18,714 Btu/lb	18,376 Btu/lb
Higher Heating Value	ASTM D 240-02	152,272 Btu/gal	149,046 Btu/gal
Total Carbon	ASTM D 5373-02	87.12% (wt/wt)	90.17% (wt/wt)
Total Hydrogen	ASTM D 5373-02	11.44% (wt/wt)	9.55% (wt/wt)
Total Nitrogen	ASTM D 5373-02	0.22% (wt/wt)	0.24% (wt/wt)

^a Analysis not performed

The quantity of trace elements in the co-processed fuel oil is still being determined. As reported previously [1], solid fuels are easily digested and analyzed via inductively coupled plasma atomic adsorption spectroscopy (ICP), cold vapor atomic adsorption spectroscopy (CVAAS), and graphite furnace atomic adsorption spectroscopy (GFAAS). Liquid fuels are not so easily analyzed due to their combustive nature in analytical techniques, which use flame spectroscopy. In addition, many of the elements traditionally analyzed in coal are not routinely analyzed in oil as they are either not present or are present in minute quantities. Two samples of the petroleum-derived fuel were originally submitted to Staveley Services/CTC Analytical Services, Portland, Oregon for analysis. Duplicate fuel oil samples were analyzed in addition to NIST Standard Reference Material (SRM) 2722 (Mercury in Crude Oil-Heavy Sweet).

Analyses were conducted according to ASTM Method D5184 (Standard Test Methods for Determination of Aluminum and Silicon in Fuel Oils by Ashing, Fusion, Inductively Coupled Plasma Atomic Emission Spectrometry, and Atomic Absorption Spectrometry (ICP AAS)) (ASTM Method D5184). The analysis of the duplicate samples is given in **Table 4-2**.

Table 4-2. Chemical Analysis of the Petroleum-Derived and Co-Processed Fuel Oils

Element	Concentration (ppm)			
	Petroleum-Derived Fuel Oil (Commercial Lab)	Petroleum-Derived Fuel Oil (Commercial Lab)	Petroleum-Derived Fuel Oil (Microwave Digestion Tech.)	Co-processed Fuel Oil (Microwave Digestion Tech.)
Al	34.0	31.6	11.89	< 0.346
As	3.63	<0.01	< 0.425	< 0.346
Ba	0.38	0.73	36.09	20.09
Be	NA ^a	NA	< 0.425	< 0.346
Cd	0.27	0.2	< 0.425	< 0.346
Co	NA	NA	2.12	1.39
Cr	0.12	0.03	0.425	< 0.346
Cu	0.16	0.96	< 0.425	< 0.346
Hg	0.59	0.13	ND ^b	ND
Mn	0.15	0.39	6.37	1.73
Mo	0.07	0.01	3.40	2.42
Ni	40.5	44.6	1.27	< 0.346
Pb	0.12	0.6	0.42	0.346
Sb	NA	NA	2.12	0.346
Se	1.40	2.18	1.27	0.693
Sr	NA	NA	1.27	0.693
V	116	129	10.19	2.42
Zn	1.46	2.08	2.12	< 0.346

^aNA Not available

^bND None detected

There is question as to the accuracy of the petroleum-derived fuel oil analysis since there are discrepancies in the concentration reported for the two samples, *i.e.*, As, Hg, Cr, and Pb. In addition, the Hg concentration reported for the NIST SRM was 1,240 ppb; however, the certified value for the SRM is 129.2 ppb. It is no surprise that the Hg data was incorrect given that the commercial lab used ICP AAS to analyze for Hg. Traditionally, mercury is best analyzed by CVAA. ICP MS has also been used for

mercury analysis. The poor agreement of the As concentration can also be attributed to the fact that As is best analyzed by GFAAS.

It was decided that a better sample preparation technique and analysis was needed to analyze metals in the fuel oils. The University of North Dakota Energy and Environment Research Center recommended a microwave digestion technique that might be appropriate for liquid hydrocarbons. The petroleum-derived and co-processed fuel oils were “digested” using the microwave procedure outlined in Appendix A and then analyzed by ICP for multi-metals and CVAAS for mercury. Chemical analysis of the fuel oils is given in **Table 4-2**.

The results of the petroleum-derived fuel oil analysis using the microwave digestion were not in agreement with the commercial lab results. In fact, the duplicate results from the commercial lab were in greater agreement than with the microwave digested sample. The analysis of the co-processed fuel was not satisfactory either since many of the metals were present at or below detection limits of the ICP at Penn State. No mercury was detected in either of the oil samples. A comparison of the microwave-digested fuel oil analyses on a lb/10¹² Btu basis with emissions measured for the respective fuels shows that there is a significant discrepancy between the total mass input of each element as compared to the emissions measured just prior to the baghouse (see **Table 4-3**). There is greater confidence in the emissions data based on our experience (over 50 emission tests using the sampling train) than on the ability of the laboratories to duplicate the fuel analysis data.

While the analysis of the fuel oil is not ideal, it does not compromise the results of the emissions data. It does limit our ability, however, to perform a material balance with confidence and determine the fate of trace metals during the refinery process. Therefore, another approach is being taken to evaluate the use of a Finnigan Element ICP-MS (high-resolution) to directly analyze organic solutions (in this case liquid hydrocarbons including RCO and LCO) [4-3]. It has been suggested that xylene may be able to be used as a “solvent” and then directly atomize the solution into the Finnigan to measure trace metals. Future plans are to develop a protocol to analyze trace metals in RCO, LCO and the various feed products given that the addition of RCO into the feedstream incorporates trace metals that may have an impact on emissions compliance.

Table 4-3. Comparison of the Concentration of Trace Metals in Fuels and Emissions

Element	Lb/10 ¹² Btu			
	Petroleum-Derived Fuel Oil	Petroleum-Derived Fuel Oil Emissions (2B)	Co-processed Fuel Oil	Co-processed Fuel Oil Emissions (3A)
Al	635.3	1239.14	< 18.8	36419.10
As	< 22.7	14.17	< 18.8	224.08
Ba	1,928.7	23.67	1,093.3	187.35
Be	< 22.7	0.23	< 18.8	12.09
Cd	< 22.7	0.19	< 18.8	1.21
Co	113.5	43.04	75.4	48.35
Cr	22.7	4.73	< 18.8	69.32
Cu	< 22.7	17.38	< 18.8	62.89
Hg	ND	0.26	ND	2.09
Mn	340.4	10541.12	94.2	8629.09
Mo	181.5	2.88	131.9	122.89
Ni	68.1	1024.00	< 18.8	117.26
Pb	22.7	4.87	18.8	1580.45
Sb	113.5	15.85	18.8	27.41
Se	68.1	3.27	37.7	6.85
Sr	68.1	23.37	37.7	122.89
V	544.6	2531.41	131.9	227.64
Zn	113.5	77.78	< 18.8	617.79

Subtask 4.2. Fuel Atomization

It is expected that the quality of atomization will influence the combustion performance and emissions because the droplet size affects the subsequent rate of oil volatilization and combustion downstream of the atomizing nozzle. Similar to measurements performed on the baseline No. 6 fuel oil, testing was planned to quantify the atomization performance of the co-processed fuel oil under the same operating conditions used for the combustion testing. Unfortunately, an insufficient amount of oil was available to perform both the atomization and combustion testing.

Factors, which affect a fuel oil's quality of atomization, include not only the flow rate and pressure of the oil and atomizing steam, but also the oil's viscosity. As reported in **Table 4-1**, a kinematic viscosity of 152 Saybolt Seconds Universal (SUS) was measured for the co-processed fuel oil at a temperature of 100°F. This viscosity was slightly higher than the 138 SUS measured for the baseline No. 6 fuel oil at approximately 210°F, the temperature to which the baseline oil was preheated for combustion testing. Therefore, without the opportunity to perform atomization testing on

the co-processed fuel oil, it was estimated that heating the co-processed fuel oil to 110°F would yield approximately the same viscosity and thus comparable atomization performance. This is the temperature that was then targeted for the co-processed fuel oil emissions testing.

Subtask 4.3. Watertube Boiler Combustion Tests

4.3.1 Description of the Research Boiler and Ancillary Equipment

Penn State's research boiler and ancillary equipment are shown in **Figure 4-1**. The 1,000 lb saturated steam (@ 150 psig)/h boiler is an A-Frame watertube boiler, designed and built by Cleaver Brooks. The combustion chamber is a 3x3x7 ft (63ft³) chamber with a maximum heat release rate of 42,000 btu/ft³-h. It contains 288 ft² of heating surface and the maximum firing rate is two million Btu/h (60 Hp).

Figure 4-1. Schematic diagram of the research boiler system.

The boiler is equipped with eighteen side ports for gaseous and particulate sampling. Fourteen of the ports have diameters of 3 inches and four have diameters of 4 inches. The combustion gases split into two convective sections, one on each side of the radiant combustion chamber. There are access doors into each of the convective sections. There are also two ash hoppers under each convective section and a doorway giving access into the radiant combustion chamber.

During testing, the steam pressure is maintained constant at 100 psig by a back-pressure regulator. The steam flow rate is measured at the outlet of the steam drum by a steam flow meter before passing through a condenser. The condensed steam then flows into a feedwater tank before returning to the boiler.

To promote and enhance combustion, a ceramic burner throat extends the combustion chamber by two feet. This ceramic section, termed a quarl, is preheated by a natural gas flame prior to introducing the fuel oil. The quarl aids in the support of the fuel's ignition by storing some of the radiant heat energy released by the flame.

Similar to the No. 6 fuel oil, the co-processed fuel oil was preheated and transported to the fuel oil gun for introduction into the boiler. High-pressure steam was also taken from the boiler's main steam drum and fed into the oil gun providing the energy to atomize the oil. A Micro-Motion Mass Flow Meter monitored the oil and atomizing steam flow rates, while the fuel oil temperature was recorded by a thermocouple located at the inlet to the oil gun. A diagram of the feed system is shown in **Figure 4-2**.

The same commercially available oil gun used with combustion testing of the baseline No. 6 fuel oil was used in testing the co-processed fuel oil. This was a type-T oil gun manufactured by Faber Burner Company in Lock Haven, Pennsylvania. A diagram of the Faber oil gun is provided in **Figure 4-3**.

A type SLC internal-mix atomizer was connected to the outlet end of the oil gun and was drilled out to an angle of 30°. This spray angle was chosen to prevent impingement of the oil droplets on the refractory-lined burner throat (quarl) during the subsequent combustion testing. It is also important that the spray angle be chosen such that the fuel droplets are entrained in the swirling combustion air stream. This ensures

that they are brought in contact with oxygen in the preheated air as well as with the hot recirculated products of combustion.

Figure 4-2. Flow diagram of the fuel oil feed system.

A gas-fired combustion air preheater supplies over 300,000 Btu/h to preheat up to 1,200 lb/h of air to 350°F. The preheated combustion air (primary air) was passed through a conventional swirl ring several inches before the gas distribution ring, both of which are 8 inches in diameter. A small portion of unheated primary air was fed through an annulus gap surrounding the nozzle. Preheated secondary air was introduced into the quarl tangentially through two headers that were balanced for uniform flow. The percentages of air introduced as cooling, primary, and secondary used in this study were approximately 2, 75, and 23, respectively.

Figure 4-3. Schematic diagram of the Faber oil gun.

The flue gas composition (O_2 , CO_2 , CO , NO_x , and SO_2) was monitored using a continuous emissions monitoring system. After leaving the boiler, the combustion products passed through an economizer and a baghouse for the removal of particulate matter. Additional sampling ports have been added to the inlet and outlet ducting of the baghouse per EPA Method 1. All instrumentation readings were recorded by a microcomputer data acquisition system.

4.3.2 Fuel Oil Combustion Test Results

A combustion performance test burning the baseline No. 6 fuel oil and the co-processed fuel oil was performed on the research boiler during this reporting period. The operating conditions (*i.e.*, atomizing steam pressure, firing rate, *etc.*) were similar to those used for the baseline No. 6 fuel oil testing performed previously [1]. A summary of the average operating conditions and combustion data for all tests are provided in **Table 4-4**.

At the beginning of each test, the quarl was heated to a temperature of approximately 1,200°F burning natural gas. The boiler was then switched to firing the baseline No. 6 fuel oil. Burning the baseline No. 6 fuel oil prior to the co-processed fuel oil on 05/24/05 allowed the system to stabilize after the transition from burning natural gas before introducing the co-processed fuel oil. This step was important given the limited quantity of the co-processed fuel oil available. It also provided an additional set of comparison data burning the baseline fuel oil.

Table 4-4. Summary of Average Boiler Operating Conditions

Fuel Type	Baseline Fuel Oil	Baseline Fuel Oil	Baseline Fuel Oil	Baseline Fuel Oil	Co-processed Fuel Oil
Test Date	6/16/04	7/7/04	7/7/04	5/24/05	5/24/05
Test Duration (h)	6.0	7.0	5.5	1.75	1.25
Flows					
Fuel Feed Rate (lb/h)	79.8	79.8	79.8	79.5	82.8
Firing Rate (MMBtu/h)	1.49	1.49	1.49	1.45	1.52
Total Combustion Air Rate (lb/h)	1,502	1,581	1,543	1,248	1,290
Cooling Air (lb/h)	24	24	24	24	24
Primary Air (lb/h)	1,135	1,183	1,176	1,022	1,055
Secondary Air (lb/h)	343	374	343	202	211
Steam Production (lb/h)	1,080	1,070	1,099	1,063	1,098
Atomizing Steam (lb/h)	71	75	74	75	74
Temperatures (°F)					
Primary Air	356	349	352	346	348
Secondary Air	618	582	599	661	668
Quarl Top	1,208	1,361	1,306	1,299	1,347
Fuel Oil	208	211	206	199	134
Flue Gas Composition (dry)					
O ₂ (%)	3.8	4.0	3.9	3.9	3.9
CO @ 3% O ₂ (ppm)	148	138	123	87	45
CO ₂ @ 3% O ₂ (%)	14.8	13.4	13.9	13.7	13.8
SO ₂ @ 3% O ₂ (ppm)	553	302	306	545	42
NO _x @ 3% O ₂ (ppm)	539	582	NA	308	87
Boiler Efficiency (%)	72.3	71.8	73.3	71.0	71.6

Similar excess oxygen levels were maintained in the flue gas for all tests performed. The reduction in the carbon monoxide levels observed burning the co-processed fuel oil relative to the tests burning the baseline No. 6 fuel oil would typically indicate an improvement in the oil's combustion efficiency. However, there is insufficient information to draw this conclusion. The most noticeable change in the emissions is the large reduction in both the sulfur dioxide (SO₂) and oxides of nitrogen

(NO_x) when burning the co-processed fuel oil. These changes are apparent in **Figure 4-4** where the emissions, corrected to 3% oxygen, are plotted as a function of time for testing performed on 05/24/05. The decrease in the sulfur dioxide levels can be attributed to the smaller amount of sulfur contained in the co-processed fuel oil relative to the baseline fuel oil. As reported in **Table 4-1**, the weight percent sulfur in the No. 6 and co-processed fuel oils is 0.93 and 0.02 wt.%, respectively.

It is unlikely that the reduction in the NO_x emissions noted during combustion of the co-processed fuel oil is fuel related (*i.e.*, fuel NO_x) because the co-processed fuel oil nitrogen content is similar to the nitrogen content in the No. 6 fuel oil. The decrease in NO_x emissions when firing the co-processed fuel oil must reflect a decrease in thermal NO_x, which may have resulted from preheating the co-processed fuel oil to a lower temperature.

The thermal efficiency of the watertube boiler was determined for each test in accordance with the input-output method as described in the ASME Power Test Codes for Steam Generating Units – Section 4.1 [4-4]. The efficiency for this method is expressed by the following equation:

$$\text{Boiler Efficiency (\%)} = \frac{\text{Output}}{\text{Input}} = \frac{\text{Heat adsorbed by working fluids}}{\text{Heat in fuel} + \text{heat credits}} \times 100$$

The results of these calculations are reported in **Table 4-4**.

The efficiency for the three days of burning the baseline No. 6 fuel oil varied between 71.0 and 73.3%, while the efficiency determined when burning the co-processed fuel oil on 5/24/05 was 71.6%. Since the efficiency for the co-processed fuel oil lies within the spread of efficiencies determined for the baseline fuel oil, there appears to be no differences in boiler performance between the two fuel oils.

Figure 4-4. Emissions (on a 3% O₂ basis) as a function of time for testing on May 24, 2005.

4.3.3 Emission Testing of Co-Processed Fuel Oil

4.3.3.1 Sampling Procedure and Analytical Methodology

The metal emissions sampling and recovery procedure during combustion testing of the co-processed fuel oil was performed using the PSU Method, which is a combination of the procedures outlined in the EPA Method 29 and Ontario Hydro Mercury Speciation Methods. EPA Method 29, Determination of Metals Emissions from Stationary Sources, was used to measure trace elements in the gas and particulate phases of the flue gases generated during coal combustion [5]. The Ontario Hydro Method is used to determine the speciation of mercury, *i.e.*, elemental and oxidized [6]. Modification of the Ontario Hydro train included omission of one KCl impinger and one $\text{H}_2\text{SO}_4/\text{KMnO}_4$ impinger and the addition of a $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger. The PSU Method is shown schematically in **Figure 4-5**. The configuration was based on discussions with University of North Dakota Energy and Environmental Research Center and testing conducted at Penn State. The recovery protocol for the filter, filter rinse, $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{SO}_4/\text{KMnO}_4$ samples are the same for Method 29 and the Ontario Hydro Mercury Speciation Method. The recovery and sample preservation of the KCl solution followed the Ontario Hydro Mercury Speciation Method.

Figure 4-5. PSU Method sample train.

The sampling position of the train downstream of the combustor, prior to the baghouse, was in accordance with EPA Method 1 (Sample and Velocity Traverses for Stationary Sources) as shown in **Figure 4-1**. The traverse sampling locations within the duct were modified from EPA Method 1 to include a horizontal traverse consisting of 4

equidistant points. Total volume of gas sampled was 61.7 actual cubic feet (Method 29 specifies 60 actual cubic feet) over a period of 93 minutes.

The sample preparation, *i.e.*, digestion, and analytical techniques for the multielements and mercury for the current PSU Method are shown in **Figure 4-6**. One solid (filter) and three liquid samples (combined KCl impingers, combined HNO₃/H₂O₃ impingers and combined H₂SO₄/KMnO₄ impingers) are generated during each test and analyzed as indicated in **Figure 4-6**. A detailed discussion of sample preparation and analysis for the PSU Method and EPA digestion methods is presented elsewhere [4-7, 4-8, 4-9].

Figure 4-6. Sample preparation and analytical techniques for PSU Method sample train.

4.3.3.2 Results and Discussion

The metals that are routinely associated with coal are not necessarily present or present in low-levels in petroleum-derived fuel oil. For example, at the end of the 1990's, 6.6 tons mercury/yr was being emitted by stationary oil combustion and 48 tons/yr was being emitted by stationary coal combustion [4-10]. The greater emission rate of coal-fired plants is attributed to the higher levels of mercury in coals. The mercury content of coals can average from 0.07 to 0.12 ppm depending upon the rank (lignite to bituminous coal). Most coals contain approximately 0.1 ppm mercury (ten times as much mercury as in oil) whereas crude oil averages about 10 ppb.

On March 15, 2005, EPA issued the first ever Federal rule to permanently cap and reduce mercury emissions from coal-fired power plants. When fully implemented in 2018, mercury emissions will be reduced from 48 tons/yr to 15 tons/yr, a reduction of 15%. A question that co-processing coal by-products and oil refinery products raises is – Will oil-fired power plants be subjected to the same regulations as coal-fired plants if coal is a feedstock in producing fuel oil? About 10 billion gallons of residual fuel oil are consumed annually in the United States [4-11]. Of this total, approximately 6, 3, and 1 billion gallons are consumed in the utility, industrial, and commercial sectors, respectively [4-11].

The mercury emitted from oil combustion represents about 10% of the U.S. yearly emission rate of atmospheric mercury from coal and oil combustion combined. However, this could change with the integration of coal into the processing/production of liquid hydrocarbon fuels. The emissions of mercury from fuel oils derived from petroleum and coal will exhibit mercury concentrations that reflect the concentration of mercury in the parent crude oil as well as any mercury or other trace elements that are extracted from the coal during processing. Therefore it is essential that there be an accurate way to measure the levels of trace elements in these fuels to determine if they pose any environmental threat thereby compromising the fuel.

To address this concern, a comparison of the emissions produced during combustion of petroleum-derived fuel oil and co-processed fuel oil is necessary. All emission tests were conducted under the same operating conditions and sampled as outlined in the previous section. Details of the petroleum-derived fuel oil combustion tests can be found in a previous semiannual report [4-1].

Emissions results for three combustion tests using a No. 6 fuel oil and one combustion test using a co-processed fuel oil are given in **Table 4-5** and **Figures 4-7 and 4-8**. Detailed results are given in Appendix B. In general, the concentration of metals (*i.e.*, As, Ba, Be, Cd, Cr, Cu, Hg, Mo, Sb, Sr, Al, Pb, Zn) in the emissions measured for the co-processed fuel oil is greater than that measured during combustion of the petroleum-derived fuel oil. Only Ni and V are consistently present in higher levels in the petroleum-derived fuel oil than in the co-processed fuel oil. Co and Se are present in

similar levels given the variability of the measurement of those elements in the petroleum-derived fuel oil.

Table 4-5. Combustion test emissions for No. 6 fuel oil and co-processed fuel oil (lb/10¹² Btu)

Element	Emissions (lb/10 ¹² Btu)			
	Petroleum-Derived Fuel Oil (1A)	Petroleum-Derived Fuel Oil (2A)	Petroleum-Derived Fuel Oil (2B)	Co-processed Fuel Oil (3A)
Al	2809.33	918.70	1239.14	36419.10
As	20.13	24.22	14.17	224.08
Ba	37.07	16.67	23.67	187.35
Be	0.42	0.16	0.23	12.09
Cd	0.41	0.14	0.19	1.21
Co	39.78	38.61	43.04	48.35
Cr	9.18	3.87	4.73	69.32
Cu	10.84	15.75	17.38	62.89
Hg	0.80	0.29	0.26	2.09
Mn	237.16	62.42	10541.12	8629.09
Mo	3.27	4.47	2.88	122.89
Ni	892.00	991.93	1024.00	117.26
Pb	12.72	9.27	4.87	1580.45
Sb	13.32	14.78	15.85	27.41
Se	7.78	1.94	3.27	6.85
Sr	43.61	13.23	23.37	122.89
V	2345.70	2311.23	2531.41	227.64
Zn	106.19	77.57	77.78	617.79

The metals present at higher concentrations in the co-processed fuel oil emissions are metals that are typically found in coal. It might be assumed that the processing of the coal to form the liquid hydrocarbon (*i.e.*, RCO) results in the incorporation of the metals into the liquid phase. Ni and V are traditionally not present in coal in significant amounts but are present in crude oil. This may account for the higher concentration of Ni and V in the petroleum-derived fuel oil emissions.

The manner in which the mercury occurs in the flue gas, *i.e.*, gas phase or associated with the particulate, is given on a percentage basis in **Figure 4-9**. In general, oxidized mercury is more problematic since it is water-soluble and tends to react with surface water to form methylated mercury. No comment can be made at this time regarding the manner in which mercury is present in the flue gas with respect to the petroleum-derived and co-processed fuel oils.

Figure 4-7. Elemental emissions for petroleum-derived and co-processed fuel oils (Part 1).

Figure 4-8. Elemental emissions for petroleum-derived and co-processed fuel oil (Part 2).

Figure 4-9. Mercury speciation measured in emissions for petroleum-derived fuel oil and co-processed fuel oil.

The data indicate that it is necessary to study how and why certain metals are incorporated into or partitioned between co-processed liquid hydrocarbon products to determine their environmental impact upon utilization. This is especially true in light of more stringent mercury regulations in the coal-fired power plant industry, which may also be imposed upon the oil-fired industry if coal or coal by-products become feedstocks for fuel oil production.

4.3.4 Upgrading Data Acquisition System

The data acquisition system (DAS) for the research boiler was upgraded in order to provide more accurate readings for some parameters, which in turn are used to calculate boiler efficiencies. Some parameters were manually obtained from pressure gauges and flow meters and then used to determine mass and energy balances. By upgrading the DAS on the research boiler, nearly all parameters are continuously monitored by the DAS, which results in more accurate averaging of test variables. Pressure transmitters were installed to measure high and low steam pressure, liquid fuel pressure at the fuel gun, atomizing media pressure, secondary air static and differential (*i.e.*, across an orifice plate) pressures, and primary air static pressure. In addition, a relative humidity sensor and boiler surface temperature probe were installed.

4.4 Acknowledgements

The following staff and students are acknowledged for their assistance in analyzing samples, preparing and recovering sampling trains, performing the combustion/emissions testing, and reducing data: Mr. Bradley Maben, Ms. Paula Smith, and Mr. Ronald S. Wasco.

Appendix A. Total Mercury Determination in Crude Oil by Microwave Digestion and Cold Vapor Atomic Absorption Spectrometry

Instrumentation

- *Microwave:*

A Model MDS-2100 microwave oven (CEM Corporation) with the temperature control probe was used. The power range, (maximum 950W), of the oven was adjusted to ramp in 1% increments. Since sample decomposition consists of several separate stages of control, the microwave is also equipped with a removable 6-position carousel. 100 ml Teflon Heavy Duty Vessels (HDV), rated to a maximum 600 psi pressure, were used.

- *Mercury Analyzer:*

A CETAC Inc. M6000A automated mercury analyzer was used to measure mercury in the digested solutions.

Reagents and Standards

Ultra trace metal grade concentrated nitric and concentrated hydrochloric acids were used. Analytical grade SnCl_2 , $\text{Mg}(\text{ClO}_4)_2$ as drying reagent, and mercury standards were used.

Procedure

- *Microwave Digestion*

Place approximately 0.5 gram of crude oil, accurately weighed to 0.001 gram, in a HDV with 5 ml of concentrated nitric acid added. Cap and place the digestion

vessels in the microwave and run heating stage one. Put the digestion vessels through additional heating steps, (heating stage 2 and 3), until the solution is clear, (light yellow in color). Add 2.5 ml of concentrated hydrochloric acid and dilute the solution to 25.0 ml with DI water in volumetric flask. Filter the solution and run on the CVAA mercury analyzer using matrix matched standards.

- *Cold vapor Atomic Absorption Mercury Analyzer*

In general, gas flow affects sensitivity. Higher gas flows always shorten the washout time, improve the signal profile shape and give less sensitivity. Low gas flow (below 80ml/minute) only be used for determination of samples contain less than 0.1ppb of mercury.

The CETAC mercury analyzer used for mercury analysis in crude oil was setup for low level mercury analysis. The sample uptake time was 60 second, the rinsing time was 140 second and the gas flow was 40 ml/minute.

- *Quality Control and Quality Assurance*

Allow the mercury lamp to equilibrate about two hours, and perform a four point calibration. Analyze a quality control standard (made from a different source of calibration standard) immediately after instrument standardization to verify the calibration accuracy.

Analyze a calibration check standard every tenth sample. If a check standard does not read within 10% of the expected value, recalibrate the instrument. Analyze a sample spike every tenth sample as well as for each different matrix to

verify analyte recovery. Run a digestion blank and one standard reference material along with the samples for quality assurance.

Table 1. Instrumental Precision

	Chevron Crude Oil, ng/L	Mandan Crude Oil, ng/L
reading # 1	21.4	80.1
reading # 2	21.9	79.8
reading # 3	21.6	80.2
reading # 4	21.4	79.9
reading # 5	21.8	80.2
reading # 6	21.3	80.0
reading # 7	21.6	80.1
% RSD	1.03	0.19

% RSD was calculated from 7 readings of same solution

Crude Oil Digestion Step 1

Stage	(1)	(2)	(3)	(4)
Power	25	35	40	40
PSI	50	80	120	120
Time(min)	10	10	30	60
TAP(min)	1	1	20	60
Temperature ° C	100	130	150	160
Fan	100	100	100	100

Crude Oil Digestion Step 2

Stage	(1)	(2)	(3)	(4)
Power	40	45	50	50
PSI	160	160	160	160
Time(min)	10	10	30	30
TAP(min)	1	1	30	60
Temperature ° C	130	150	170	190
Fan	100	100	100	100

Crude Oil Digestion Step 3

Stage	(1)	(2)	(3)	(4)
Power	40	45	50	50
PSI	160	160	160	160
Time(min)	10	10	30	30
TAP(min)	1	1	20	60
Temperature ° C	130	150	170	190
Fan	100	100	100	100

Crude Oil Digestion Step 4

Stage	(1)	(2)	(3)	(4)
Power	60	60	60	60
PSI	160	160	160	160
Time(min)	10	10	30	30
TAP(min)	1	1	20	60
Temperature ° C	130	150	170	190
Fan	100	100	100	100

Appendix B. Sampling Parameters and Sample Train Analyses

Test No:	RI-PSU-1A					Sampling Parameters			Isokineticity Calc.			
Test Date:	06/16/2004					Total H2O (g):	451.9		Vw(std): SCF	21.420		
Fuel Type:	#6 Fuel Oil					Total Dust (g):	1.8747		VmC: ACF	123.379		
Cal. Value						Pb (in Hg):	29.9		Vm(std): SCF	115.422		
(Btu/lb)	18,714					Delta H (in H2O):	0.696		Vt(std): SCF	136.842		
						Tm (R):	567		% H2O:	15.65		
						Ts (R):	808		Vs: FM	1436.295		
Firing Rate:						Ps (in Hg):	29.2		Qn: ACFM	0.765		
lbs/hr	79.8					Delta P (in H2O):	0.084		Qn(std): SCFM	0.489		
Btu/hr	1,493,377.0					Cp:	0.99		% Isokinetic:	114.13		
						Dn (in):	0.3125					
PSU Method	Total Volume or					Total Vm (ACF):	122.582		Dust Loading Calc.			
Sample Train	Weight Collected					Sample Time (min):	245		DCL: (grains/scf)	0.2114		
Splits	(mL or g)					Duct Dia: (ft)	0.625		Stack Flow: ACFM	440.426		
Rinse & KCl	1000								Stack Flow: SCFM	281.879		
H ₂ O ₂	500											
KMnO ₄	500											
Filter	1.8747											
Test 1A Lab Analysis Data - Uncorrected for Split Size (volume or mass)						Test 1A Lab Analysis Data - Corrected Totals						
Analyte	Rinse & KCl (µg/L)	H ₂ O ₂ (µg/L)	KMnO ₄ (µg/L)	Filter (µg/filter half)		Rinse & KCl (µg)	H ₂ O ₂ (µg)	KMnO ₄ (µg)	Filter (µg)	Total (µg)	Total Emissions (lb/10 ¹² Btu)	
Al	1030	14.6		7180		1030	7.30		14360	15397.30	2809.33	
As	72.8	1.48		18.4		72.8	0.74		36.8	110.34	20.13	
Ba	18.8	0.384		92.1		18.8	0.19		184.2	203.19	37.07	
Be	ND	ND		1.14		ND	ND		2.28	2.28	0.42	
Cd	ND	ND		1.11		ND	ND		2.22	2.22	0.41	
Co	ND	ND		109		ND	ND		218	218	39.78	
Cr	11.3	5.60		18.1		11.3	2.80		36.2	50.30	9.18	
Cu	5.27	1.89		26.6		5.27	0.95		53.2	59.42	10.84	
Hg	2	< 0.4	2	0.7031		2	< 0.2	1	1.4062	4.4062	0.80	
Mn	886	454		93.4		886	227.00		186.8	1299.80	237.16	
Mo	ND	ND		8.95		ND	ND		17.90	17.90	3.27	
Ni	108	1.75		2390		108	0.88		4780	4888.88	892.00	
Pb	ND	0.614		34.7		ND	0.31		69.4	69.71	12.72	
Sb	ND	ND		36.5		ND	ND		73.0	73.00	13.32	
Se	29.0	4.11		5.79		29	2.06		11.58	42.64	7.78	
Sr	31.0	ND		104		31	ND		208	239	43.61	
V	95.7	1.12		6380		95.7	0.56		12760	12856.26	2345.70	
Zn	151	22.0		210		151	11.00		420	582.00	106.19	
Test Oil												
Analyte	(mg/kg or ppm)	(lb/10 ¹² Btu)										
Al	34.0	1,817										
As	3.63	193.97										
Ba	0.38	20.31										
Be	1.19	63.59										
Cd	0.27	14.43										
Co	2.65	141.61										
Cr	0.12	6.41										
Cu	0.16	8.55										
Hg	0.59	31.53										
Mn	0.15	8.02										
Mo	0.07	3.74										
Ni	40.5	2,164.2										
Pb	0.12	6.4										
Sb	NM	NM										
Se	1.40	74.8										
Sr	NM	NM										
V	116	6,199										
Zn	1.46	78.0										

Task 5. Pitch and Coke Material

The objective of this part of the research program is to optimize the routes identified where coal introduced into the delayed coker results in coke of higher value that can be used towards carbon anodes or graphite electrodes, along with providing useful liquid streams for liquid fuels and binder pitch. The froth flotation stream of tertiary coal cleaning facilities has been identified as a potential source of feedstock for co-coking. However, to ensure a good interaction between the coal and the heavy petroleum residue, several factors associated with coal rank needs to be evaluated due to differences in volatile matter, degree of plasticity, heteroatom and mineral matter content. Isolation of vitrinite macerals with very low mineral content is an objective that will ensure a feed material of a high degree of plasticity that will become an integrated part of the resultant coke. Additional beneficiation will be needed to obtain this objective. The resultant cokes and pitches of the optimized coal will be tested for their application towards carbon products using a range of test capabilities at Penn State University as well as in cooperation with industry.

Good progress was made during the past year in surmounting the technical difficulties of attempting to make premium carbon products (coke and pitch materials) from RCO/LCO mixtures or from co-coking coal and petroleum residues in our laboratory delayed coker. In particular, our efforts have been directed at generating a suitable clean coal product from Pittsburgh seam froth flotation cell samples to generate sufficient coke and pitch distillate fraction from our laboratory delayed coker to test and study. The following is a summary of the research that has been completed during this performance period

Summary

Samples of as-mined coal and of froth flotation products from a Consol Energy, Inc. mine in Washington County Pennsylvania were obtained. The Pittsburgh seam coal was selected because it is a high volatile A bituminous of relatively high vitrinite content and thermoplastic properties. There are at least four million-plus tons per year mines in southwestern Pennsylvania that employ advanced cleaning technology, and therefore represents a potential supply of materials for co-coking. The froth flotation effluent (FCE) was selected because it deals with the beneficiation of the natural fines generated from the mining process and because it tends to concentrate the vitrinite portion of a coal which is also responsible for most of a coal's thermoplastic properties. However, because FCE generally contains significant ash yield secondary cleaning procedures were investigated and developed to generate a 1.0 % ash yield product to be used for our first coker feed. About 16 kg of coke was produced from 12 consecutive runs using 20 weight percentage of the clean Pittsburgh FCE in our laboratory-scale delayed coker. The coke product has been supplied to A.J. Edmond Co. for calcining. Providing that the calcined coke meets the requirements, it will be provided to Alcoa as a potential coke product for anode use in the aluminum industry. Furthermore, a pitch product has been isolated by distillation from the heavy distillate from an early co-coking experiment. Characterization of these materials in comparison to a standard coal-tar and a petroleum pitch, suggests that our cut point was perhaps taken at too high a temperature and that a heat treatment may be necessary to increase the concentration of condensed aromatic-fused-ring compounds. This information will be evaluated in more detail before the large

composite distillate generated from the consecutive runs using Pittsburgh seam FCE is processed.

Subtask 5.1 Sample Procurement and Preparation

Decant oil

A heavy petroleum stream (decant oil) from United Refining is being used for the co-coking experiments, which in addition to having no ash yield, has the gross chemical properties listing in **Table 5-1**. Results from vacuum distillation given in **Table 5-2** show that about 27% of the decant oil reports to the gasoline, jet fuel and diesel boiling point range which corresponds to about the same amount of alkane, alkene, and naphthalene compounds detected in distillates [5-1]. The remainder of the decant oil is composed of phenanthrenes through pyrenes and larger aromatic molecules.

Table 5-1 Ultimate Analysis of Decant Oil [5-1]

Reading, dry basis	Decant Oil
Carbon	89.7
Hydrogen	0.3
Nitrogen	0.2
Sulfur	0.8
Oxygen	-
Ash yield	0.0

Table 5-2 Product Distribution by Weight for Vacuum Distillation [5-1]

Product Distribution by Weight from Vacuum Distillation				
Feed Material	IBP-180°C gasoline	180-270°C jet fuel	270-332°C diesel	332-FBP°C fuel oil
Decant Oil	5.99	11.41	9.22	72.14

Coal

During this report period evaluation of the cleaning potential of the Pittsburgh seam froth flotation cell effluent (FCE) samples obtained from Mine No. 84/Eighty Four Mining owned and operated by CONSOL Energy Inc. in Washington Co., PA was performed. Three individual samples were collected, one on January 21, 2004 for an initial evaluation and two additional samples of approximate 500 kg were collected on November 23, 2004 and May 31, 2005 to produce a clean coal product for coke and distillate production.

Testing of the initial froth flotation cell sample showed that by removing the <45 μm size fraction (-325 mesh) the ash yield of the coal product could be reduced from about 15% to about 3.0%. However, to make a premium quality carbon product ash yield would have to be reduced further. Consequently, a study of the influence of different specific gravity liquids on coal product quality was undertaken and a quantity of several clean coal products were made for evaluation in the laboratory-scale delayed coker.

Once completed a plan was developed to generate sufficient clean coal product to produce a significant quantity of coke (about 16 kg) and distillate to provide samples to make carbon artifacts for subtask 5.6 and to generate a binder pitch for subtask 5.5. The plan involved collecting two new Mine No. 84 froth flotation cell product that, when thoroughly cleaned would provide about 20 kg of coal for 12 consecutive coker runs. A new frother sample (about 500 kg) was collected on November 23, 2004 and different procedures were applied to attempt to clean such a very large sample through February. It was determined that more sample would be required to generate our gross coal sample and a second 500 kg frother cell effluent sample was collected on May 31, 2005.

Preparation and Evaluation of the Initial Sample (January 21, 2004)

Originally, two sample types were collected from Mine No. 84, i.e., a bulk coal sample and a sample from the froth flotation cells. The bulk 50 x 0 mm size sample was crushed to -6 mm and processed for the Penn State Coal Sample Bank and received a designation “DECS-34”, whereas the froth flotation cell samples were eventually combined into a large composite sample from which the <45 μm size fraction was removed. The analytical characteristics of these samples are compared with samples from previous work in **Table 5-3**. Results show that by increasing the degree of cleaning improvement was seen in the concentration of thermoplastic coal macerals and a reduction in the ash yield. However, ash yield needed to be reduced further (below 1.0%) and there appeared to be a reduction the thermoplastic properties. Because of this a study was undertaken to determine the influence density separation would have on the ash yield and desirability of further cleaning.

It was determined that a 150 μm x 45 μm split of the frother cell product was necessary for proper feeding into the delayed coker. Manual wet sieving of the original froth cell sample yielded 31% of this size fraction. The dry ash content of this size fraction was 3.1% with a dry sulfur content of 1.2%. Washability tests (ASTM D4371-91 (1988), [5-3] were conducted at five different specific gravities to lower the ash content of the froth, i.e., at 1.40, 1.35, 1.30, 1.29 and 1.28 g/ml.

Once these tests were completed, the total remaining mass of the +45 x -150 μm size fraction of the original froth flotation sample was combined and floated in two

density solutions, i.e., 1.302 and 1.279 g/ml specific gravity. As seen in **Table 5-4**, there was a marked decrease in the ash yield of each specific gravity fraction with a

Table 5-3 Analytical Characteristics of Coal Samples Used in Co-coke Experiments

Analytical Procedure	Whole Clean Powellton	Re-cleaned Powellton Froth	Powellton /Eagle EI107	Pittsburgh Seam DECS-34	Pittsburgh Froth >45 - <150 μ m
Proximate Analysis: (dry)					
Fixed Carbon, %	65.1	68.7	64.6	54.3	61.7
Volatile Matter, %	29.9	29.4	27.3	38.4	35.2
Ash, %	5.0	1.9	8.1	7.4	3.1
Ultimate Analysis: (dry)					
Carbon, %	87.6	86.3	80.9	78.2	82.6
Hydrogen, %	5.8	5.2	4.6	5.2	5.7
Nitrogen, %	1.6	1.5	1.3	1.6	1.5
Sulfur, %	0.9	0.9	nd	1.6	1.2
Oxygen, % (diff)	4.1	6.1	nd	6.0	5.9
Gieseler Plastometer:					
Softening Temperature, (C)	385	387	397	381	nd
Fluid Temperature Range (C)	103	105	88	91	nd
Maximum Fluidity (ddpm)	30,000	23,619	7,002	16,418	nd
Temperature at Maximum (C)	448	448	446	435	nd
Particle Size Distribution:					
D[v,0.9], microns	nd	152	nd	nd	89
D[v,0.5], microns	nd	61	nd	nd	22
D[v,0.1], microns	nd	10	nd	nd	5
Ash Mineral Composition:					
Silicon Dioxide, %	51.43	45.16	nd	48.47	nd
Aluminum Oxide, %	30.53	25.43	nd	23.15	nd
Ferric Oxide, %	9.04	12.68	nd	14.84	nd
Titanium Oxide, %	1.49	5.58	nd	1.00	nd
Phosphorus Pentoxide, %	0.13	0.10	nd	0.53	nd
Calcium Oxide, %	1.80	3.56	nd	2.49	nd
Magnesium Oxide, %	0.62	1.51	nd	0.76	nd
Sodium Oxide, %	0.77	0.34	nd	0.69	nd
Potassium Oxide, %	2.40	2.51	nd	1.87	nd
Sulfur Trioxide, %	1.05	3.49	nd	1.95	nd
Organic Petrography:					
Total Vitrinite, %	68.0	88.1	86.5	82.8	90.3
Total Liptinite, %	8.6	2.0	1.4	4.0	7.7
Total Inertinite, %	23.4	9.9	12.1	13.2	2.0

concomitant increase in the amount of those petrographic entities that possess thermoplastic properties (vitrinite and liptinite). However, there was a marked decrease in the maximum fluidity and the fluid temperature range of both specific gravity fractions which may have an impact on coke quality. At this stage of experimentation where manual methods are employed for clean coal separation and the coal must be thermally dried between steps, a certain amount of oxidation and loss of thermoplastic properties can be expected; this should be eliminated when the process is automated.

Table 5-4 Comparison of Different Fractions of the Initial and Final Pittsburgh Seam Test Sample

Analytical Procedure	Different Fractions of Mine #84 Pittsburgh Seam Samples				
	DECS-34 2 x 0 Fraction	DECS-34 -150 μ m	1.302 Float +45 μ m FCE	1.279 Float +45 μ m FCE	1.280 Float FCE EI#186
Coker Run #	-	41, 44	45	46	55
Proximate Analysis: (dry)					
Fixed Carbon, %	54.3	nd	nd	62.9	63.4
Volatile Matter, %	38.4	nd	nd	36.1	35.6
Ash, %	7.4	nd	1.6	1.0	0.99
Ultimate Analysis: (dry)					
Carbon, %	78.2	nd	nd	82.6	84.6
Hydrogen, %	5.2	nd	nd	4.8	5.3
Nitrogen, %	1.6	nd	nd	1.8	1.6
Sulfur, %	1.6	nd	nd	1.0	1.1
Oxygen, %	6.0	nd	nd	8.8	6.4
Gieseler Plastometer:					
Softening Temperature, (C)	381	382	388	385	385
Fluid Temperature Range, C	91	90	80	87	93
Maximum Fluidity (ddpm)	16,418	20,668	1,841	3,612	29,527
Temperature at Maximum,C	435	436	433	430	436
Organic Petrography:					
Total Vitrinite, vol. %	82.8	90.3	93.9	95.2	96.2
Total Liptinite, vol. %	4.0	2.0	2.8	2.2	1.5
Total Inertinite, vol. %	13.2	7.7	3.3	2.6	2.3

New Mine No. 84 Pittsburgh Seam Froth Flotation Samples

To fulfill the obligations of the other subtasks of Task 5.0 regarding the need for sufficient coke to make a carbon artifact as well as the need for sufficient liquid products to determine product distribution (specifically to make a binder pitch), new and larger coal samples would be needed. The plan included making 12 consecutive coker runs using the 80% decant oil to 20% coal ratio which would require about 20 kg of cleaned coal material. Thus, on November 23, 2004 a new froth flotation cell sample was obtained from Mine No. 84. However, this sample was different from the former in that a de-watered effluent sample from the combined output of the frother cells was desired. Raw feed to Mine No. 84's eight froth flotation cells is approximately 80 tons per hour with a 45% product yield. Unfortunately, there was no direct access point to the de-watered stream after the centrifuge bowls; the only way to obtain the desired sample was to skim the top coal layer from a traveling belt. In order to obtain a representative froth sample, ASTM D 6609-01, Condition C-2, was followed to the extent possible [5-3]. The skim sample was taken in ten 30-gallon containers over about a four hour period and grossed about 530 kg. A series of tests were conducted in December to determine the amount of time and man-power that might be required to obtain a 1.279 specific gravity fraction of the 100 x 325 mesh (150 x 45 μm) size fraction employing the manual techniques used on the original sample. It was determined that at least 258 man-days would be required and that another technique had to be devised.

To automate the process of collecting such a narrow particle size range, a Derrick Model K Vibrating Screen Machine was employed. It is a combination vibrating/wet

sieving apparatus that utilizes two nested 58"l x 17.5"w screens, one with openings of 150 μ m and the other with 45 μ m openings. The screens were adjusted to an angle 15° from horizontal and were vibrated at 3600 cycles per minute through a horizontal displacement of approximately 0.25 inches. A high-pressure spray of water is maintained across the entire screen width and is adjusted so the frother product will remain in the water stream for approximately 5 seconds. The >150 μ m, 150 μ m x 45 μ m, and <45 μ m splits were collected. The >150 μ m split was reintroduced to the device for a second washing. The 150 μ m x 45 μ m split was likewise reintroduced for a second washing. Particle size distribution data (ASTM D 4749-87(2002) e1, [5-3] show the effectiveness of the Derrick apparatus; less than 1% of >150 μ m material and less than 2% of <45 μ m material was retained in the 150 μ m x 45 μ m split. Manual wet sieving gives similar results.

The splits were dried in a Despatch drying oven set at 54°C (130°F) with approximately 6 air changes per minute. As with the initial frother cell sample washability tests were completed on the intermediately cleaned skim-belt material to find that a 1.280 g/ml specific gravity solution would be required to obtain a <1% dry ash product. After this test series it was found that a second skim-belt sample of about 500 kg would be required to produce the required amount of clean coal product using this technique. Consequently, another sample was collected in May 2005. Processing was completed and separate aliquots for the coking runs were prepared by mid-July. As shown in **Table 5-4**, properties of the 1.280 float FCE sample (designated EI#186) compared well with the 1.279 float +45 μ m FCE evaluation sample showing slightly better thermoplastic properties and organic composition. By concentrating the vitrinite

component of the coal there was some concern that there might be a preference for only the higher reflecting, less thermoplastic layers of vitrinite from the coal. **Figure 5-1** compares the maximum reflectance distribution of the bulk Pittsburgh seam sample (DECS-34) with the cleaned product which shows that there are no significant differences in the vitrinite population.

Figure 5-1 Comparison of the Maximum Vitrinite Reflectance Distributions of the Bulk Pittsburgh Seam Sample (DECS-34) and the Clean Coal Product (EI#186)

Subtask 5.2 Examine the Resid from Fractionation of the Deeply-Hydrotreated RCO/LCO as a Pitch Material

Large quantities of higher boiling material have been obtained as a result of the large-scale production of all materials for this project as described in Task 1 of this report. It is expected that removal of light components from the heavier fraction will be done during the first half of year three of the project.

Subtask 5.3 Co-Coking of Coal and Heavy Petroleum Stream

A description of the laboratory scale coking apparatus and the hydrotreated versions of refinery produced decant oil are described in detail in Task 1 of this report. The process conditions for a series of co-coking runs with Powellton/Eagle coal are also described in Task 1 of this report.

Subtask 5.4 Analysis of Co-Coking Coke

Concluded in the 2004 Annual Report [5-2] was the fact that the remnants of coal were being concentrated in the lower half and toward the center of the coke artifact taken from the laboratory scale delayed coker. If this were to happen in an industrial scale delayed coker it might lead to blockages, production delays and would most certainly influence the uniformity of coke quality. Therefore, research was performed to characterize the inhomogeneity and quality of a “typical” coke discharge from the coker and to evaluate what influence operating conditions, such as feed rate and bath temperature, might have on the inhomogeneity.

Following the experimental and analytical procedures given in the 2004 Annual report [5-2], coke discharges from four different coker runs were sectioned at various intervals from the inlet and evaluated using optical microscopy and proximate analysis (moisture, volatile matter, ash yield and fixed carbon). One coke, from Run #15 (a run very similar to Run #14 using 20% Powellton coal, [5-2]) was sectioned for proximate analyses at various intervals and then the whole carbon artifact was crushed to pass 1.18 mm sieve (16 mesh) and homogenized for additional characterization. Two other cokes (#41 and #44, Table 5-5), which were generated using 20% Pittsburgh seam coal (DECS-34) that had been crushed to pass 150 μm sieve (100 mesh), were evaluated by optical microscopy and compared with Run #35 that was included in the 2004 Annual Report [5-2]. Run #55 (Table 5-5), which represents a mid-point coking run in the series of 12 runs to generate a suitable coke for testing for the aluminum industry, was sectioned for both proximate analysis and petrography.

Evaluation of Run #15 Coke

Coker Run #15 employed a 4:1 blend of decant oil and Powellton Coal (EI-107) and was operated under the same conditions as Run #14, except that it was steam stripped for one hour before cooling. One-centimeter thick sections were cut from the 45 cm long 8.0 cm diameter coke artifact at the 1-2 cm, 12-13 cm and 24-25 cm levels above the inlet. Subsections from each disk of coke were cut from the outer rim (A) and interior (B) to compare the proximate analysis (ash and volatile matter yield). The remainder of the coke was crushed to pass a 1.18 mm sieve (16 mesh), homogenized and packaged in

about 350 g aliquots. A small subsample was split from the total mass for proximate and petrographic analysis the results of which are found in **Tables 5-6 – 5-8**.

Table 5-5 – Conditions and Yields from the Experimental Delayed Coker

Conditions	Run #35	Run #41	Run #44	Run #45	Run #46	Run #55
Date	7/8/04	10/5/04	11/10/04	11/16/04	12/1/04	8/30/05
Components	4:1 Decant Oil/+45 μ m Pittsburgh Froth	4:1 Decant Oil/-150 μ m DECS-34 Pittsburgh	4:1 Decant Oil/-100 μ m DECS-34 Pittsburgh	4:1 Decant Oil/1.302 float of Pittsburgh Flotation Sample	4:1 Decant Oil/1.279 float of Pittsburgh Flotation Sample	4:1Decant Oil/1.280 float of Pittsburgh FCE EI#186
Feed, hrs	6	3	6	6	6	6
Held at 500°C, hrs	6	24	24 (@550°C)	24 (@550°C)	24 (@ 550°C)	24
Feed Rate, g/min	16.7	33.4	16.7	16.7	16.7	16.8
Preheater inlet, °C	108	63	120	123	120	121
Preheater Outlet, °C	443	441	425	431	430	439
Coke Drum Inlet, °C	468	478	470	470	476	499
Coke Drum Low/mid., °C	469	473	471	469	473	498
Coke Drum Top, °C	470	477	475	472	476	479
Total Feed, g	4931	5388	6256	6100	6040	6054
Coke Product, g (%)	1491 (30.2%)	1602 (29.7%)	1677 (26.8 %)	1757 (28.8 %)	1263 (20.9 %)	1660 (27.4 %)
Liquid Product, g, (%)	2976 (60.4%)	3268 (60.6 %)	3675 (58.7 %)	3636 (59.6 %)	4263 (70.6 %)	3813 (63.0 %)
Gas Product, g, (%)	464 (9.4 %)	518 (9.6 %)	904 (14.5 %)	707 (11.6 %)	514 (8.5 %)	581 (9.6 %)

As can be seen in **Table 5-6**, the interior sections (B) had a greater amount of ash and volatile matter yield than those from the outer sections (A) at any given level. Also, there was a slight decrease in ash yield with increasing distance from the inlet. These data correlate well with the petrographic information that showed that the remnants of coal were concentrated toward the bottom and center of the delayed coker as

demonstrated by the summary in **Table 5-7**. Evaluation of the composite sample (**Tables 5-8 and 5-9**) showed that on a whole-coke basis about half of the coal-derived entities have been enhanced and that on a volume percentage basis the proportions of petroleum- and coal- derived carbon textures were about equal. Furthermore, an evaluation

Table 5-6 Proximate Analysis of Run #15 Coke from Different Levels Above the Inlet

Sample Id.	% Moisture	% Ash, dry	% Volatile Matter, dry	% Fixed Carbon, dry	Sulfur
1-2 cm, A	1.89	9.28	8.15	82.57	nd
1-2 cm, B	2.41	15.02	9.86	75.12	nd
12-13 cm, A	1.23	5.03	7.27	87.70	nd
12-13 cm, B	2.30	11.76	9.61	78.63	nd
24-25 cm, A	1.02	2.97	7.31	89.72	nd
24-25 cm, B	2.25	12.77	9.92	77.32	nd
Whole Coke	1.13	6.65	7.18	86.17	0.45

of major and some trace elements was completed on the whole coke composite sample which found that 98% of the 6.5 % ash yield was composed of 72.8% SiO₂, 17.8% Al₂O₃, 2.74% Fe₂O₃, 1.68% TiO₂, 1.01% K₂O, 0.98% Na₂O, 0.84% MgO, 0.46 % CaO and less than 0.1% BaO, MnO, P₂O₅, SrO, and V₂O₅.

One of the main reasons for looking at the whole-coke properties of Run #15 was to determine if the coke product we produce might make a reasonable fuel/reductant for coal-based direct reduction (of iron) technology. In partnership Kobe Steel and Midrex have developed a new coal-based DRI process, i.e., Ironmaking Technology Mark Three, or ITmk3, that employs low volatile coal. Because of the worldwide shortage of low volatile coal for cokemaking it was suggested that delayed coke made with added coal

might make a useful substitute if the sulfur and phosphorous content can be minimized. A 350g sample of 1.18 mm was shipped to John Kopfle of Midrex Technology, Inc. in September, 2004 and the sample was passed on to Kobe Steel for evaluation and reactivity testing. At presently, we have yet to receive feedback.

Distribution of Ash and Volatile Matter Yield in Other Cokes

The distribution of volatile matter and ash yield at different levels within other coke artifacts was of interest and results can be found in **Table 5-10**. Regardless of the starting ash yield of the coal, the highest concentration of mineral matter appeared to be at the bottom center of the coke artifact and decreased in concentration from the inlet. The volatile matter content was considerably more variable, but tended to be greater toward the center of the artifact and was influenced greatly by soak temperature which was 550°C for Run #44 compared with 500°C for the other sample listed in **Table 5-5**.

Table 5-7 - Petrographic Summary of the Percentage Coal and Petroleum Derived Coke Textures (Vol. %) in Coker Sample #14

Location	% Coal-derived	% Petroleum-derived
From Bottom, cm		
1 – 2 cm	80.1	19.9
6 – 7 cm	80.9	19.1
12 – 13 cm	80.1	19.1
18 – 19 cm	68.7	31.3
24 – 25cm	74.5	25.4
Radial Section, mm		
0 – 13 mm	40.9	59.1
13- 29 mm	75.8	24.2
29 – 54 mm	96.2	3.8

Table 5-8 – Petrographic Analysis of Carbon Textures in a Composite of Coker Sample #15 by Size and Origin, Vol. %

Sample Id.	Vitrinite-derived		Inert-derived	Isotropic Vitrinite	Min. Matter	Isotropic Petroleum derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
	Enhanced	Non-enhanced								
Composite	22.2	17.1	7.3	0.4	1.3	0.1	11.2	31.9	7.3	1.2

Table 5-9 – Proportion of Textures Derived from Coal and Decant Oil Compared with the Normalized Concentration of Decant Oil Textures in Composite Coke from Run #15, Vol. %

Sample Id.	% Coal-derived	% Petroleum-derived	Isotropic Petroleum-derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
Composite	48.3	51.7	0.2	21.7	61.7	14.1	2.3

Table 5-10 Proximate Analysis of Coke from Different Levels Above the Inlet in Other Coke Artifacts

Sample Id.		% Moisture	% Ash, Dry	% Volatile Matter, dry	% Fixed Carbon, dry
Run #14, 20% Powellton Coal, 8.1 % Ash Yield					
1 – 2 cm	Outer	0.68	4.56	7.05	88.39
	Inner	1.54	13.91	10.77	75.32
12 – 13 cm	Outer	0.75	5.16	7.46	87.38
	Inner	1.22	12.31	9.73	77.96
24 – 25 cm	Outer	0.77	3.54	7.51	88.95
	Inner	1.05	10.33	9.85	79.82
Run #35, >45 μm <150 μm Pittsburgh Seam FCE, 3.1 % Ash Yield					
1 – 2 cm	Outer	0.78	2.70	8.95	88.35
	Inner	0.94	7.47	9.85	82.68
12 – 13 cm	Outer	0.59	1.17	8.54	90.29
	Inner	0.70	1.73	8.81	89.46
24 – 25 cm	Outer	0.40	0.11	7.96	91.93
	Inner	0.42	0.12	7.96	91.92
Run #44, - 100 mesh (<150 μm) Pittsburgh Seam Coal (DECS-34), 7.4% Ash Yield					
1 – 2 cm	Outer	1.07	7.11	6.11	86.78
	Inner	1.30	12.17	7.37	80.46
12 – 13 cm	Outer	1.13	1.81	5.78	92.41
	Inner	1.28	4.98	6.67	88.35
24 – 25 cm	Outer	1.12	2.50	5.90	91.60
	Inner	1.21	3.71	7.47	88.82
Run #55, 1.280 float Fraction of Pittsburgh Seam FCE, 0.99 % ash Yield					
1 – 2 cm	Outer	1.26	1.38	7.44	91.18
	Inner	1.42	3.25	7.55	89.20
12 – 13 cm	Outer	1.27	0.39	6.97	92.64
	Inner	1.17	0.53	8.89	90.58
24 – 25 cm	Outer	1.15	0.69	7.03	92.28
	Inner	1.25	1.06	6.64	92.30

Influence of Operating Conditions on Coke Textures

Inspection of the coke discharged from the laboratory delayed coker using optical microscopy demonstrated that a large majority of the coal remnants were being retained at the bottom of the reactor. For the Powellton coal approximately 77% of the carbon in the lower 25 cm of the coke discharge was coal-derived as summarized in **Table 5-7**. Several ideas were advanced regarding the concentration of coal that included settling under the force of gravity sometime during the process to the agglomeration of thixotropic coal particles within the highly fluid decant oil causing a phase separation. Because the viscosity regimes within the reaction vessel during the six hours of filling are unknown, it seemed unlikely that large-scale settling could be occurring during the period in which material was being pumped into the vessel at 16.7 g/min. It seems more likely that phase separation would occur as the slightly sticky and thermoplastic coal particles enter the reaction vessel; the larger particles agglomerate, while the highly fluid decant oil and smaller coal particles pass upward into the vessel interior.

From earlier petrographic work [5-2], it was apparent that a certain amount of the vitrinite-derived carbon had been influenced by contact with the decant oil, that is, the optical textures were nearly twice as large compared with the same vitrinite coked in the absence of decant oil. In radial section the enhancement of the vitrinite-derived textures was more prominent toward the outside of the carbon artifact and non-enhanced vitrinite was found more toward the interior. The relative geometry of vitrinite enhancement suggests limited exposure to the decant oil during the period of coal particle fluidity, resulting either from proximity or duration of the coal's fluid temperature range. Consequently, two experiments were designed using the Pittsburgh seam bulk sample

(DECS-34) crushed to pass 150 μm (100 mesh) that would double the feed rate (Run #41) or would increase the bath temperature (Run #44) of the decant oil/coal blend to preheat the coal particles (hopefully, preheating would reduce the thermal gradient within the refractory coal particles and extend their thermoplastic range).

As discussed in the 2004 Annual Report [5-2], coke artifacts from each delayed coker run were removed as a single cylinder of coke, cut into sections from which exterior and interior samples could be removed to prepare samples for reflected-light optical microscopy. Point count analyses using the carbon textures previously identified were performed on all sections of coke from the two new runs and are compared with those from Run #35 in **Tables 5-11 – 5-16**. A summary of the distribution of coal- and petroleum-derived carbon textures is provided in **Table 5-17**. Briefly, without regard to reaction conditions there was a fairly high concentration of coal-derived carbon textures in the lower part of the coke artifact from the delayed coker and in Runs #41 and #44 most of the vitrinite-derived carbon has seen significant enhancement of carbon textures. Those carbon textures derived from the decant oil increased in concentration and size as distance increased from the inlet, particularly for Runs #35 and #41.

Table 5-11– Petrographic Analysis of Carbon Textures in Coker Sample #35 by Size and Origin, Vol. %

Long. Interval, cm	Cross Section, mm	Vitrinite-derived		Inert- derived	Isotropic Vitrinite	Min. Matter	Isotropic Petroleum derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
		Enhanced	Non- enhan.								
1.0 – 2.0	0.0 – 27.5	37.5	0.4	5.4	0.0	1.1	0.3	46.3	8.8	0.2	0.0
	27.5 – 49.2	20.3	40.5	18.6	0.0	1.6	0.9	16.1	2.1	0.0	0.0
6.0 – 7.0	0.0 – 25.5	44.4	1.5	4.4	0.0	0.5	0.7	34.3	13.4	0.7	0.1
	25.5 – 41.0	7.7	42.5	34.9	1.7	2.3	2.2	7.8	0.8	0.1	0.0
12.0 – 13.0	0.0 – 19.8	17.9	0.5	2.2	0.0	0.5	0.1	31.8	42.5	4.5	0.0
	19.8 – 41.2	20.0	0.4	3.8	0.0	0.7	0.0	43.5	30.2	1.4	0.0
18.0 – 19.0	0.0 – 15.1	3.4	0.0	0.6	0.0	0.1	1.0	18.0	61.4	14.0	1.5
	15.1 – 35.6	0.0	0.0	0.0	0.0	0.0	1.1	5.9	70.5	19.4	3.1
24.0 – 25.0	0.0 – 17.7	0.0	0.0	0.0	0.0	0.0	1.4	4.1	78.8	12.7	3.0
	17.7 – 36.4	0.0	0.0	0.0	0.0	0.0	1.9	5.2	72.2	18.0	2.7

Table 5-12 – Proportion of Textures Derived from Pittsburgh Seam Coal and Decant Oil Compared with the Normalized Concentration of Decant Oil Textures in Coke from Run #35, Vol. %

Long. Interval, cm	Cross Section, mm	% Coal- derived	% Petroleum- derived	Isotropic Petroleum- derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
1.0 – 2.0	0.0 – 27.5	44.4	55.6	0.5	83.8	15.8	0.4	0.0
	27.5 – 49.2	81.0	19.0	4.5	84.5	11.0	0.0	0.0
6.0 – 7.0	0.0 – 25.5	50.8	49.2	1.4	69.8	27.2	1.4	0.2
	25.5 – 41.0	89.1	10.9	20.2	71.6	7.3	0.9	0.0
12.0 – 13.0	0.0 – 19.8	21.1	78.9	0.1	40.3	53.9	5.7	0.0
	19.8 – 41.2	24.9	75.1	0.0	57.9	40.2	1.9	0.0
18.0 – 19.0	0.0 – 15.1	4.1	95.9	1.0	18.8	64.0	14.6	1.6
	15.1 – 35.6	0.0	100.0	1.1	5.9	70.5	19.4	3.1
24.0 – 25.0	0.0 – 17.7	0.0	100.0	1.4	4.1	78.8	12.7	3.0
	17.7 – 36.4	0.0	100.0	1.9	5.2	72.2	18.0	2.7

**Table 5-13 – Petrographic Analysis of Carbon Textures in Coker Sample #41 that Used -100 Mesh DECS-34
at Double the Flow Rate (33.4 g/min) by Size and Origin, Vol. %**

Long. Interval, cm	Cross Section, mm	Vitrinite-derived		Inert- derived	Isotropic Vitrinite	Min. Matter	Isotropic Petroleum derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
		Enhanced	Non- enhan.								
1.0 – 2.0	0 – 25	82.5	0.2	9.6	0.1	1.9	0.1	5.6	0.0	0.0	0.0
	25 – 49	87.9	0.3	8.5	0.1	0.6	0.0	2.6	0.0	0.0	0.0
6.0 – 7.0	0 – 25	80.0	0.5	7.6	0.0	0.8	0.1	10.9	0.1	0.0	0.0
	25 – 48	73.8	8.1	10.2	0.0	0.9	0.3	6.7	0.0	0.0	0.0
12.0 – 13.0	0 – 19	65.3	1.1	7.2	0.0	1.4	0.2	22.5	2.3	0.0	0.0
	19 – 38	68.7	1.5	7.6	0.0	0.7	0.6	19.7	1.2	0.0	0.0
18.0 – 19.0	0 – 22	20.5	0.8	3.9	0.0	1.4	0.1	23.4	44.7	3.6	1.6
	22 – 49	1.6	0.0	0.8	0.0	0.0	0.9	5.9	73.3	15.4	2.1
24.0 – 25.0	0 – 26	0.4	0.0	0.9	0.0	0.0	1.7	4.2	72.8	17.2	2.8
	26 – 56	0.1	0.0	0.7	0.0	0.0	1.6	3.1	71.5	21.5	1.5

**Table 5-14 – Proportion of Textures Derived from Pittsburgh Seam Coal (-100 Mesh DECS-34) and Decant Oil Compared
with the Normalized Concentration of Decant Oil Textures in Coke from Run #41, Vol. %**

Long. Interval, cm	Cross Section, mm	% Coal- derived	% Petroleum- derived	Isotropic Petroleum- derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
1.0 – 2.0	0 – 25	94.3	5.7	1.8	98.2	0.0	0.0	0.0
	25 – 49	97.4	2.6	0.0	100.0	0.0	0.0	0.0
6.0 – 7.0	0 – 25	88.9	11.1	0.9	98.2	0.9	0.0	0.0
	25 – 48	93.0	7.0	4.3	95.7	0.0	0.0	0.0
12.0 – 13.0	0 – 19	75.0	25.0	0.8	90.0	9.2	0.0	0.0
	19 – 38	78.5	21.5	2.8	91.6	5.6	0.0	0.0
18.0 – 19.0	0 – 22	26.6	73.4	0.1	31.9	60.9	4.9	2.2
	22 – 49	2.4	97.6	0.9	6.0	75.1	15.8	2.2
24.0 – 25.0	0 – 26	1.3	98.7	1.7	4.3	73.8	17.4	2.8
	26 – 56	0.8	99.2	1.6	3.1	72.1	21.7	1.5

Table 5-15 – Petrographic Analysis of Carbon Textures in Coker Sample #44 that Used a Higher Mix-Bath Temperature by Size and Origin, Vol. %

Long. Interval, cm	Cross Section, mm	Vitrinite-derived		Inert-derived	Isotropic Vitrinite	Min. Matter	Isotropic Petroleum derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
		Enhanced	Non- enhan.								
1.0 – 2.0	0.0 – 19.0	57.8	9.8	5.6	0.0	0.5	0.0	20.0	6.0	0.1	0.1
	20.0 – 42.0	37.1	43.2	10.7	0.1	1.3	0.3	6.9	0.4	0.0	0.0
6.0 – 7.0	0.0 – 19.0	18.1	0.6	1.9	0.0	0.5	0.6	12.9	58.2	6.5	0.7
	20.0 – 40.2	14.9	5.0	3.6	0.0	0.4	0.5	13.1	57.2	3.6	1.7
12.0 – 13.0	0.0 – 21.0	8.7	0.5	1.5	0.0	0.0	0.4	8.3	72.2	7.5	0.9
	22.0 – 47.0	6.3	8.9	4.0	0.0	0.9	0.6	8.8	60.3	7.3	2.9
18.0 – 19.0	0.0 – 21.5	8.9	3.6	3.3	0.0	1.5	0.5	8.8	66.9	4.5	2.0
	22.5 – 47.2	3.6	6.5	3.2	0.0	0.2	0.7	8.3	71.2	5.5	0.8
24.0 – 25.0	0.0 – 27.0	8.4	0.1	1.8	0.0	0.0	0.4	5.7	70.7	7.6	5.3
	28.0 – 55.0	13.6	0.3	2.9	0.0	0.0	0.3	7.3	69.3	4.2	2.1

Table 5-16 – Proportion of Textures Derived from Pittsburgh Seam (DECS-34, -100 Mesh) and Decant Oil Compared with the Normalized Concentration of Decant Oil Textures in Coke from Run #44 that Use a Higher Mix-Bath Temperature, Vol. %

Long. Interval, cm	Cross Section, mm	% Coal-derived	% Petroleum-derived	Isotropic Petroleum-derived	Mosaic, <10 μ m	Small Domain, 10-60 μ m	Domain >60 μ m	Flow Domain, >60 μ m L, <10 μ m W
1.0 – 2.0	0.0 – 19.0	73.7	26.3	0.0	76.2	22.8	0.5	0.5
	20.0 – 42.0	92.4	7.6	4.0	90.8	5.2	0.0	0.0
6.0 – 7.0	0.0 – 19.0	21.1	78.9	0.8	16.3	73.8	8.2	0.9
	20.0 – 40.2	23.9	76.1	0.6	17.2	75.3	4.7	2.2
12.0 – 13.0	0.0 – 21.0	10.7	89.3	0.5	9.3	80.8	8.4	1.0
	22.0 – 47.0	20.1	79.9	0.8	11.0	75.5	9.1	3.6
18.0 – 19.0	0.0 – 21.5	17.3	82.7	0.6	10.7	80.9	5.4	2.4
	22.5 – 47.2	13.5	86.5	0.8	9.6	82.3	6.4	0.9
24.0 – 25.0	0.0 – 27.0	10.3	89.7	0.4	6.4	78.8	8.5	5.9
	28.0 – 55.0	16.8	83.2	0.4	8.8	83.3	5.0	2.5

Table 5-17 – Summary of Percentage Coal- and Petroleum- Derived Coke Textures (Vol. %) at Different Locations in the Delayed Coke Artifact for Pittsburgh Seam Coals as a Function of Feed Rate and Bath Temperature

Interval Above Inlet, cm	Run #35		Run #41		Run #44	
	% Coal-derived	% Petro.-derived	% Coal-derived	% Petro.-derived	% Coal-derived	% Petro.-derived
Feed Rate, g/min	16.7		33.4		16.7	
Bath Temp. °C	108		63		120	
1.0 – 2.0	60.5	39.5	95.4	4.6	83.9	16.1
6.0 – 7.0	67.4	32.6	89.1	10.9	22.5	77.5
12.0 – 13.0	23.1	76.9	76.8	23.2	15.9	84.1
18.0 – 19.0	1.7	98.3	13.3	86.7	15.2	84.8
24.0 – 25.0	0.0	100.0	1.0	99.0	13.6	86.4

In terms of the influence of reaction conditions on the homogeneity of coke textures, some information can be seen in **Table 5-17**, but other information comes from qualitative observations. Most of the coal-derived carbon textures found in Run #35 (+45 μm Pittsburgh froth sample) remained in the lower 40% of the artifact. Using a slightly different coal material in the new experiments (one with more mineral matter and inertinite coal macerals which might cause settling or retention at the bottom of the reactor), the feed rate was doubled for Run #41 with the hope that coal materials would be pushed higher into the reaction vessel and would counter materials settling. As seen in **Table 5-17**, a large proportion of the coal-derived carbon was found in the lower 30% of the reaction vessel. Furthermore, visual inspection of the coke artifact showed that a large proportion of deformed shot coke-like particles represented the lower 2 cm of the artifact. Although the rounded particles were flattened and deformed their presence was not unexpected as shot coke tends to form in highly turbulent dynamic environments within commercial delayed cokers [5-4]. The shot-like particles were composed of mosaic textures derived largely from the petroleum fraction. In general, the coke textures

from the exterior to interior and from above 2.0 cm were fairly well mixed and certainly more uniformly distributed than those observed in Run #35. However, high feed rate does not result in a uniform or homogeneous coke product.

Run #44 was designed to see what influence preheating of the coal might have on increasing the thermoplastic properties of coal, thus improving the contact time between coal and decant oil. The benefits of preheating coal charges above 200°C for coke making and for increasing chloroform extractability have long been known [5-5, 5-6]. Even preheating in the range of 100 – 135 °C has some benefits for removing moisture, decreasing coking time by 30%, and allowing the use of marginal coking coals in coal blends. Some of the reasons for these empirical observations can be placed upon improved heat transfer (i.e., energy is no longer required to drive off moisture can be applied to heating the carbonaceous fraction) and the fact that the carbonaceous fraction has been heated 20% of the way to the thermoplastic range. This may not mean that thermoplasticity is actually measurably improved, but that we are allowing coal at the peak of its thermoplasticity to contact the decant oil. In the current experiment decomposition of the decant oil, beginning at 120°C, was a limiting factor. The decant oil/coal blend was stirred and heated overnight before being pumped into the preheater and then to the delayed coker reaction vessel.

As shown in **Table 5-17**, there is still a high concentration of coal-derived carbon textures within the first 2.0 cm of the coke artifact, but with increasing distance from the inlet there was a significant decrease in the amount of coal-derived carbon out to 25.0 cm particularly in comparison to Runs #41 and #35. Presumably, coal remnants may be found beyond the 25 cm level. Although the work has yet to be completed, samples of

coke from the 30-31 cm and 35-36 cm levels have been prepared for petrographic evaluation. Preheating to 120°C appears to have some positive influence on the homogeneity of carbon textures, but the question remains to be, what temperature would be optimum? Conceivably, the coal could be heated to a much higher temperature (say 250°C) separately and then blended with decant oil in batches or at the last minute to avoid decomposition and premature coking of the decant oil fraction of the blend.

As the high bath temperature was applied to those runs that used deeply cleaned Pittsburgh froth (Runs #45, #46 and #55), during the next performance period these cokes will be evaluated for homogeneity of optical textures as well as proximate analysis. Furthermore, it may be possible to evaluate a slightly higher bath temperature or to preheat coal to a higher temperature, if phase separation continues to be a problem.

Subtask 5.5: Analysis of Co-Coking Binder Pitch

As discussed in the Annual Report 2004 [5-2] the liquid product from the co-coking Run #35 was further distilled to yield a pitch material. About 13% was in the pitch boiling point range (cut-point temperature of ~250°C at ~3 mmHg or ~450°C at ambient pressure). This distilled pitch was named co-coking pitch-1 or CCP-1. However, the CCP-1 sample was lost during the period of semi-annual report 2005 to the annual report 2005. Therefore, a new co-coking pitch, namely CCP-2, was distilled from the leftover fuel oil fraction from the same co-coking Run #35. The focus of the following section is on the chemical characterization of co-coking pitch using different analytical techniques (i.e. Gas Chromatography-Mass Spectrometry (GC/MS), Pyrolysis GC/MS (Py-GC/MS), High Pressure Liquid Chromatography (HPLC), Laser Desorption

Ionization/Mass Spectrometry (LD/MS), Solid State Nuclear Magnetic Resonance (Solid State NMR) and Solution State NMR) to study the molecular weight distribution, especially in the ranges of the heavy end compounds. A standard coal tar pitch (SCTP) and commercial petroleum pitch (PP) were also studied as reference materials. The aim of this research effort is to better understand pitch chemistry and its role as a good binder in the preparation of carbon artifacts.

Materials:

Co-coking pitch was obtained by using a laboratory-scale vacuum distillation apparatus. The heavy-end of the distillate sample from the co-coking process was placed in a round-bottom flask, which was connected to a riser and condenser assembly. The temperature of the boiling liquid was measured by a thermocouple. A cold trap kept in liquid nitrogen was used to collect any light product not condensed in the collection flask. After the pressure was reduced to 0.5 mmHg using a rotary-vane vacuum pump, the heating mantle was switched on. The temperature was increased and the distillates were collected until the temperature reached 450°C (at atmospheric pressure). The temperature was controlled carefully to minimize overheating and thermal degradation. The flask was weighed before and after distillation to obtain the weight fraction of residue. The distillate was measured by weighing the entire assembly before and after distillation. The co-coking pitch obtained was approximately 13% by weight of the original distillate from the co-coking unit, i.e., 87% of the distillate boiled below 450°C and 13% of the pitch materials boiled above this temperature). The standard coal tar pitch, i.e. SCTP-2, and the commercial petroleum pitch, i.e. PP-1, obtained from the

Koppers Co., Ltd. were used as reference materials. The properties of these three pitches are shown in **Table 5-18**.

Table 5-18. Properties of SCTP-2, PP-1 and CCP-1.

Property	SCTP-2	PP-1	CCP-1
Elemental Analysis			
C	93.83±0.20 [†]	93.48±0.21 [†]	91.62±1.09 [†]
H	3.87±0.16 [†]	5.55±0.44 [†]	5.91±0.65 [†]
N	1.03±0.05 [†]	0.20±0.07 [†]	0.34±0.02 [†]
S	0.56±0.01 [†]	1.21±0.08 [†]	3.34±0.09 [†]
O (by calculation)	0.71	-0.45	-0.28
C/H ratio	24.22	16.83	15.49
Metal			
Calcium (ppm)	24 [‡]	5 [‡]	N.A
Chlorine (ppm)	17 [‡]	15 [‡]	N.A
Iron (ppm)	115 [‡]	19 [‡]	N.A
Lead (ppm)	28 [‡]	N.D. [‡]	N.A
Nickel (ppm)	4 [‡]	4 [‡]	N.A
Phosphorous (ppm)	0 [‡]	N.D. [‡]	N.A
Potassium (ppm)	32 [‡]	2 [‡]	N.A
Silicon (ppm)	352 [‡]	377 [‡]	N.A
Sodium (ppm)	N.D. [‡]	54 [‡]	N.A
Vanadium (ppm)	3 [‡]	8 [‡]	N.A
Zinc (ppm)	64 [‡]	0 [‡]	N.A
Other Properties			
Softening Point (°C)	114 [‡]	111.9 [‡]	~50-60 ^{††}
Quinoline Insolubles (wt%)	15 [‡]	0.1 [‡]	N.A
Toluene Insolubles (wt%)	32.59±2.05 [†]	3.89±0.80 [†]	0.0 [†]
DCM Insolubles (wt%)	xx [†]	0.53 [†]	N.A
THF Insolubles (wt%)	34.66 [†]	3.2 [†]	N.A
Coking Value (wt%)	58.3 [‡]	47 [‡]	N.A.
Specific Gravity @ 25°C	1.34 [‡]	1.246 [‡]	N.A.
Sulfur Content (wt%)	0.56±0.01 [†]	1.21±0.08 [†]	3.34±0.09 [†]
Moisture (wt%, dry)	0.08±0.06 [†]	0.00±0.00 [†]	0.04±0.04 [†]
Volatile Matter (wt%, dry)	40.56±0.22 [†]	53.46±0.12 [†]	89.30±2.04 [†]
Fixed Carbon (wt%)	59.12±0.34 [†]	46.51±0.06 [†]	10.36±1.99 [†]
Ash Content (wt%)	0.25±0.06 [†]	0.04±0.06 [†]	0.29±0.08 [†]

N.D. = Not Detectable; N.A. = Not Available

[†] Data obtained from The Energy Institute

^{††} Approximated by viscosity measurement

[‡] Data provided by Koppers Co., Ltd

Experimental

The analytical techniques employed in this study include GC/MS, Direct Probe-Mass Spectrometry (DI-MS), Py-GC-MS, HPLC, LD/MS, Solid State NMR and Solution State NMR). Fine solid particles (>100 mesh size) were used in the Py-GC/MS. Soxhlet extraction was used to obtain a solvent-soluble from pitch samples. A viscosity measurement was also performed.

Viscosity

Viscosity measurement was performed using a Rheology International Model RI:2:M/H1/H2. The measurement was done based on ASTM D5018 and the temperature ranges were 100-200°C.

DI-MS

A QP5000 Shimadzu mass spectrometer was used with 70 eV electron ionization. The THF-solubles were concentrated by evaporating the THF using ultrapure nitrogen blowing at room temperature. The dry solid sample was dissolved in dichloromethane (DCM) to obtain 16mg solid sample per 1 mL DCM. 3 microliters of solution was injected into the probe and the solvent was dried by blowing with ultra pure nitrogen at room temperature for 20 minutes before inserting into the mass spectrometer. The interface temperature was 200°C. The sample was heated in the probe from ambient to 350°C at 20°C/min, while spectra were collected. The spectra were summed to produce one overall spectrum for each sample.

GC/MS

Analyses were performed on a Shimadzu QP5000 with 70 eV electron ionization. The GC was equipped with an XTi-5 fused silica capillary column (30m x 0.25mm. x

0.25 μ m). A 20 mg pitch sample was dissolved in 1 mL dichloromethane (DCM) and sonicate for 5 minutes in a vial with a septum. The solution was automatically injected into a GC. The temperature of the GC/MS transfer line was set at 290°C. The GC interface and injector temperatures were both held at 290°C. The temperature program applied to the GC oven was: isothermal at 40°C for 4 min; temperature programmed at 4°C/min to 320°C; isothermal at 320°C for 15 min. The mass spectrometer was operated in full scan mode (m/z 40–500 and 1 scan/s). Only co-coking pitches were analyzed by this method.

Py-GC/MS

Analyses were performed on an HP 5890 gas chromatograph series II fitted with a 5971A MSD and a CDS Analytical Pyroprobe 1000. The GC was equipped with an XTi-5 fused silica capillary column (30m x 0.25mm. x 0.25 μ m). Samples were not weighed but similar quantities were input. Samples were subjected to pyrolyze in a flow of helium (0.65 kg cm²) for 10s at a temperature of 310°C. The temperature of the GC/MS transfer line was set at 290°C. The pyrolysis interface and the GC injector were both held at 310°C. The temperature program applied to the GC oven was: isothermal at 40°C for 5 min; temperature programmed at 4°C/min to 290°C; isothermal at 290°C for 15 min.

HPLC

The THF-soluble fractions were analyzed by HPLC using a Waters system incorporated with the Pinnacle II™ PAH column from Restek USA. The Pinnacle II™ PAH stationary phase is packed with a specialized polymer with pore size 110 Å and has an average particle size of 5 μ m. A UV detector operating at 254 nm was used. The mobile phase was Acetonitrile (ACN) and Dichloromethane (DCM) at a flow rate of 1

mL·min⁻¹. The 100% Acetonitrile was fed from 0 to 20 minutes, then DCM was added linearly from 20-90 minutes and followed by 100% DCM from 90-120 minutes. An HPLC equipment (Waters Model 600E) incorporating a Waters 996 Photodiode array detector, operating between 190 and 800 nm, was used to obtain UV spectra.

Since the THF soluble obtained from the Soxhlet extraction was too dilute and the sample to be injected into the HPLC had to be soluble in the mobile phase, the sample was concentrated by evaporating the THF using the ultrapure N₂ blowing at room temperature. The dry solid sample of the THF soluble was added with DCM to obtain 16mg solid sample per 1 mL DCM. 2-5 microliters of solution was injected into the HPLC for the analysis.

LD/MS

LD mass spectra were obtained using a Micromass MALDI-L/R. The samples were sent to be analyzed by the Huck Institute, Department of Chemistry, The Pennsylvania State University. No matrix assist was used for any of these analyses. A 20 mg whole-pitch sample >200 mesh size was dissolved in 1 mL quinoline and sonicate for 5 minutes. The pitch solution was deposited on a sample well and dried before insertion in the mass spectrometer ion source.

Solid State Nuclear Magnetic Resonance (NMR)

All solid state NMR analyses were done at the School of Chemical, Environmental and Mining Engineering, the Nottingham University, United Kingdom.

A. Solid State ¹³C NMR

All ¹³C NMR measurements were carried out at ca 50.46 MHz on a Bruker MSL200 spectrometer. About 250 mg of sample was packed tightly into a zirconia rotor

and spun at 5500 rpm while acquiring the signals. Tetrakis(trimethylsilyl)silane (TKS) was used as a standard. The 90° ¹³C pulse width was 6 microseconds and a recycle delay of 5 seconds were used. A 500- and 1000-scan were performed to give a reasonable resolution at a reasonable time for cross-polarization magic-angle-spinning (CP/MAS) and simple Bloch decay or single-pulse excitation (SPE) techniques, respectively.

In the dipolar dephasing (DD) experiments were performed in both CP/MAS and SPE techniques. Nine dephasing periods of 1, 5, 10, 20, 40, 100, 200, 350 and 500 μ s were collected for CP/MAS-DD experiments while only 3 dephasing periods of 1, 60 and 500 μ s were collected for SPE-DD due to a very long experimental time.

B. Solid State High Temperature ¹H NMR

A Doty 200 MHz ¹H NMR probe was used with a Bruker MSL300 spectrometer to study the change in characteristics of pitch-only samples and the wetting characteristics of pitch + petroleum coke samples at the temperature ranges of 20-450°C. A flow of 16 L/min of dry N₂ gas was flown to transfer heat to the sample container through the bottom of the stator. A controller was used to control the temperature and an extra thermal couple was placed at the bottom of the sample container to verify the sample temperature. Below the sample region, a 60 L/min of dry air was flown to prevent the temperature rising above 50°C in order to protect the electrical components and another 20 L/min dry air was blown into the region between the top bell Dewar enclosing the sample region and the outer side of the probe to prevent the temperature from exceeding 110°C.

The sample container with its screw cap was made of boron nitride and was protected by a container holder of zirconia. The container cap contained a 0.2 mm diameter ventilation hole. The assembly was placed horizontally in the stator. Only 1/4 of container volume was filled by pitch to prevent/reduce any spill of pitch when heated at higher temperature due to its high viscosity and volume expansion. About 30-40 mg of sample was used for the “pitch only” experiment. In the pitch+coke experiment, a concentration of 22% by weight of pitch was mixed with 20-60 mesh-size petroleum coke and about 150-180 mg of the mixture was placed in the boron nitride sample container.

Solution State NMR

The solution state NMR analyses were performed at the Energy Institute, PSU.

A. Solution State ^1H NMR

Samples were analyzed on a Bruker AMX 360 NMR operating at 9.4 Tesla and 360MHz. About 30 mg of whole pitch sample ground to >200 mesh size was dissolved in 1 ml 99.8% atom deuterated chloroform which contains 1% (v/v) Tetramethylsiloxane (TMS) from Aldrich. The pitch solution was placed in a 5 mm o.d. NMR tube without filtering. A 256-scan was acquired to ensure a reasonably good sensitivity for proton spectra. A recycle time of 5 seconds was used with a 90°C pulse length of 5 μ s. The analyses were performed at 27°C. The FIDs were Fourier transformed directly and the integration was done using the Xwin NMR version 2.5 software.

B. Solution State ^{13}C NMR

The solution state ^{13}C NMR measurements were acquired at 90.56 MHz using Bruker AMX 360 NMR operating at 9.4 Tesla. About 400 mg of >200 mesh size whole

pitch sample was dissolved in 4 mL deuterated chloroform (99.8% purity which contains 1% (v/v) Tetramethylsiloxane (TMS) from Aldrich). The pitch solution was filtered using a filter paper and placed in a 5-mm o.d. NMR tube. The ^1H decoupling and spin-lock field was ca 3 kHz and 70° ^{13}C pulse width was 2.0 microseconds. The ^{13}C relaxation time constants (T_1 s) were not determined. However, Chromium (III) Acetylacetonate ($\text{Cr}(\text{AcAc})_3$; 99.99% purity purchased from Aldrich) was added to reduce the T_1 s to below 1 second. The amount of $\text{Cr}(\text{AcAc})_3$ used was 10 mg per 1 mL pitch solution. The recycle delay of 2.5 second was used and at least 15,000 scans were acquired for each sample.

Results

Viscosity

The viscosity of CCP-1, PP-1 and SCTP-2 at different temperatures are shown in **Figure 5-2**. PP-1 and SCTP-2 show comparable viscosity in the ranges of 120-210°C. As expected, the viscosity of CCP-1 was lower than those of PP-1 and SCTP-2.

Figure 5-2. Viscosity Measurement of CCP-1, PP-1 and Sctp-2.

Direct Probe MS

The DI-MS gives the overall mass distribution of the sample; as shown in **Figure 5-3**. Each figure consists of a total ion chromatogram (TIC) of the sample, and the inner chromatograms showing the select ion chromatograms (SIC). Compounds up to 9 fused rings could be analyzed. The decant oil, the parent material of the co-coking pitch, was rich in 3-4 aromatic ring compounds, and quite a few heavy aromatic compounds, especially those of 7-9 fused rings as shown in **Figure 5-3(A)**. The PP-1 and Sctp-2 (see **Figure 5-3(C)** and **Figure 5-3(D)**, respectively), which were used as reference materials, contained mostly 4-6 aromatic ring compounds. The co-coking pitch (see **Figure 5-3(B)**) also consisted of compounds in the range of 4-6 aromatic ring compounds; however, the distribution of these 4-6 fused rings was much narrower than

the SCTP-2 and PP-1. It can be observed that small compounds in the ranges of 3-4 fused rings, such as phenanthrene, anthracene and pyrene, in the co-coking pitch were mostly removed from the distillation process. These 3-4 aromatic ring compounds play an important role as a lubricant in the binder phase and suggest that the cut point of the co-coking pitch was too high. In order to recover the 3-4 aromatic ring compounds, the cut point should be decreased to recover these smaller components; however, this will lower the softening point of the pitch. On the other hand, the presence of the heavy aromatic compounds in the co-coking pitch was also much lower than those of PP-1 and SCTP-2. The heavy aromatic compounds act as a stationary phase and prevent excessive weight loss after carbonization of the carbon artifact and shift the softening point to a higher value. The softening point of the co-coking pitch was around 50-60°C (as approximated by the viscosity measurement) and needs to be increased to about 110°C in order to be used as a binder in the production of carbon artifact.

Figure 5-3

Chromatograms of (a) Decant oil; (b) CCP-1; (c) PP-1; and (d) Sctp-2 from the DI-MS. The outer chromatogram is the sum of the overall sample. The inner small chromatograms are the sum of each molecular weight as indicated in each sub-figure.

Table 5-19. Molecular Weights of Possible Aromatic Compounds Contained in Pitch Samples

MW	Possible Structure(s)	Compound Name
178.25		Anthracene
		Phenanthrene
202.25		Pyrene; Benzo(def)Phenanthrene
		Benzo(jk)fluorene; Fluoranthene; Benzene, 1,2-(1,8-Naphthylene)-; 1,2-benzacenaphthene; 1,2-(1,8-Naphthalene)Benzene
228.30		Triphenylene
		Chrysene; Benzo[a]Phenanthrene
		Benz[a]anthracene; 1,2-Benzoanthracene; 1,2-Benzanthracene
	2,3-benzanthracene; Tetracene; Naphthacene

252.30		<p>Benzo[e]Pyrene; 4,5-Benzopyrene; 4,5-Benzopyrene; 1,2-Benzpyrene; 1,2-Benzopyrene</p>
	<p>Perylene; Peri-dinaphthalene; Dibenz[de, kl]Anthracene</p>
		<p>Benzo[k]fluoranthene; Dibenzo[b, jk]fluorene; 8,9-benzofluoranthene; 2,3,1',8'-binaphthylene; 11,12-benzofluoranthene</p>
	<p>Benzo[a]pyrene; Benzo(d,e,f)chrysene; 6,7-benzopyrene; 3,4-benzpyrene</p>
276.35		<p>Benzo[ghi]perylene; Benzo[ghl]perylene; 1,12-benzoperylene</p>
	<p>Dibenzo[def,mno]chrysene; Dibenzochrysene, (anthanthrene); Ddibenzo[def, mno]chrysene; Dibenzo[cd, jk]pyrene; Anthanthrene</p>

		o-phenylenepyrene; Indeno[1,2,3-cd]pyrene
278.35		Pentacene; Lin-naphthoanthracene; Lin-dibenzanthracene; Benzo[b]naphthacene; 2,3:6,7-dibenzanthracene
	Benzo[a]chrysene; Picene; Dibenzo[a, i]phenanthrene; 3,4-benzchrysene; 1,2:7,8-dibenzophenanthrene
		Benzo[b]chrysene, 1,2:6,7- Dibenzophenanthrene; Naphth[2,1-a]anthracene; Benzo[c]tetraphene; benzo[b]chrysene; 3,4-benzotetracene; 2,3:7,8- dibenzophenanthrene; 2,3-benzochrysene; 1,2:6,7-dibenzophenanthrene
		Dibenz[a,c]anthracene; Naphtho-2',3':9,10- phenanthrene; Dibenzo[a, c]anthracene; dibenz[a, c]anthracene; Benzo[b]triphenylene; 2,3-benzotriphenylene; 1,2:3,4-dibenzoanthracene; 1,2:3,4-dibenzanthracene
300.35		Dibenzo[ghi,pqr]perylene; Dibenzo[ghi, pqr]perylene; Coronene
302.35		Benzo[rst]pentaphene; Dibenzo[a,i]pyrene; 3,4:9,10-dibenzopyrene

	<p> Dibenzo[def,p]chrysene; Dibenzo[def,p]chrysene; Dibenzo[a,l]pyrene; 1,2:3,4-dibenzopyrene </p>
	<p> Dibenzo[fg,op]naphthacene </p>
		<p> Dibenzo[a,e]pyrene; Naphtho[1,2,3,4-Def]chrysene; Dibenzo[a,e]pyrene; 1,2:4,5-dibenzopyrene </p>
326.40		<p> Nnaphtho[1,2,3,4-ghi]perylene; 1,12-phenyleneperylene </p>

350.40		Phenanthro[1.10.9.8-opqra]perylene; Meso-naphthodanthrene; Phenanthro[1,9,10,8-fghi]perylene; Phenanthro[1,10,9,8-opqra]perylene; Naphthodanthrene; Bisanthrene
352.45		Dibenzo[h,rst]pentaphane; Tribenzo[a,e,i]pyrene; 1,2,4,5,8,9-tribenzopyrene; 1,2,4,5,7,8-tribenzopyrene
376.45		Pyranthrene; Tribenzo[ghi, m, pqr]picene; Benzo[c]naphtho[3,2,1,8,7-rstuv]pentaphene; 1,2:7,8-dibenzoanthanthrene
398.45		Phenanthro[3,4,5,6-qrabc]coronene; Ovalene

426.50		Benzo[rst]phenanthro[1,10,9-cde]pentaphene
	Tetrabenzo[de, hi, op, st]pentacene
	Violanthrene; Dinaphtho[1,2,3-dc 3',2',1'-lm]perylene; Dibenzanthrene; Anthra[9,1,2-cde]benzo[rst]pentaphene, 5,10-dihydro-
428.50		Isoviolanthrene; Benzo[rst]phenanthro[10,1,2-cde]pentaphene, 9,18-dihydro-

GC/MS

Since a new co-coking pitch, namely CCP-2, was generated to replace the lost CCP-1 a comparison of GC/MS spectra of these two pitches is shown in **Figure 5-4**. It can be observed that the patterns of compounds in CCP-1 and CCP-2 are similar, however, CCP-2 spectra is shifted to lower elution times, i.e. lower temperatures. Since the GC/MS analyses of these two samples were done in different years, i.e. CCP-1 and CCP-2 were analyzed in Summer 2004 and Fall 2005, respectively, there might be some variation in the oven temperatures or contamination in the capillary column between these two analyses. Nevertheless, the GC/MS spectra confirm that both CCP-1 and -2 contain similar compounds, although CCP-2 has a tiny fraction of lighter compounds in the ranges of 230-136°C as shown in **Figure 5-4**.

Figure 5-4. A Comparison of GC/MS Spectra between CCP-1 and CCP-2.

Py-GC/MS

Figure 5-5 shows the chromatograms of CCP-2, PP-1 and Sctp-2 from the Py-GC/MS analyses. It is obvious that compounds present in Sctp were much less complicated than those in PP-1 and CCP-2. The patterns of compounds in CCP-2 were similar to PP-1, but CCP-2 compounds eluted at $\sim 240^{\circ}\text{C}$ to 290°C while PP-1 compounds eluted at 180°C - 290°C .

Figure 5-5. Chromatograms of (a) PP-1 and (b) Sctp-2 from the Py-GC/MS.

High Pressure Liquid Chromatography (HPLC)

Figure 5-6 shows chromatograms of decant oil, co-coking pitch, PP-1 and Sctp-2 from the HPLC analyses. Only result from the Sctp-2 showed good separation

between peaks. The operating conditions have to be fine-tuned in order to get good results that can be used to compare all samples. This can be done by adjusting the conditions of the mobile phase such as flowrate, rate of solvents mixing or trying different solvent to use as a mobile phase. A new analysis method was developed as shown in **Figure 5-7** and gave a fair improvement in resolution when testing with SCTP-2 (see Table). This method will be employed to analyze other samples.

Table 5-20. Analysis Program for HPLC

	Time	Flow	%ACN	%DCM	%Water	Curve*
1		0.5	40	0	60	
2	30	0.5	100	0	0	1
3	50	1	100	0	0	1
4	120	1	0	100	0	6
5	140	1	0	100	0	1
6	141	2	100	0	0	1
7	160	2	100	0	0	1
8	161	0.5	40	0	60	1
9	171	0.5	40	0	60	1

* Curve “1” = linearly increase concentration; Curve “6” = same concentration from the beginning time and sharply ramp up at the final time.

Figure 5-6. Chromatograms of (A) Decant oil; (B) CCP-1; (C) PP-1; and (D) SCTP-2 from the HPLC.

Figure 5-7. HPLC Spectra of SCTP-2 (analysis program shown in Table 5-20)

LD/MS

Figure 5-8 shows LD/MS spectra of CCP-1, PP-1 and Sctp-2. Compounds in PP-1 and Sctp-2 ranged up to >1000 amu, whereas those in CCP-1 ranged from 200-350 amu. These results obviously show that only deep vacuum distillation (the highest cut point for co-coking pitch was ~250°C at ~3 mmHg or ~450°C at ambient pressure) to produce the co-coking pitch was not enough, and a further heat treatment is needed to produce more condensed aromatic-fused-ring compounds. Lighter aromatic compounds in the ranges of 120-200°C are also needed to duplicate the compounds in Sctp.

Figure 5-8. LD/MS spectra of (A) CCP-1; (B) PP-1; and (C) Sctp-2

Solid State NMR

A. ^{13}C Solid State NMR

In the analysis of pitch by ^{13}C solid state NMR technique, co-coking pitch was not analyzed since this pitch was quite soft at room temperature and might spill and damage the probe when spinning at a very high revolution rate. However, there was a possibility to analyze a low softening point pitch by solidifying the sample to its glassy state and acquire the spectra at the glassy temperature. This possibility will be examined in the future. Hence, at room temperature, only SCTP-2 and PP-1 were analyzed. **Figure 5-9** shows CP-MAS and SPE spectra of SCTP-2 and PP-1. The aromatic peak centers at 125 ppm and the aliphatic carbon peaks distribute between 0-60 ppm. However, with the 5500 rpm spinning, the right-side aromatic sideband was located in the same region as the aliphatic peaks. The ^{13}C solid state NMR spectra will be deconvoluted to calculate the concentration of different types of carbons, e.g. non-protonated aromatic carbons, bridgehead aromatic carbons, aromaticity of the whole pitch sample, etc. This information will be useful to approximate the average ring size of aromatic compounds in pitch samples.

Figure 5-9. Solid state ^{13}C NMR Spectra of (A.1) CP-MAS Spectra of SCTP-2; (A.2) SPE Spectra of SCTP-2; (B.1) CP-MAS Spectra of PP-1; and (B.2) SPE Spectra of PP-1

B. High Temperature Solid State ^1H NMR

High temperature ^1H NMR was used to follow the changes in the proton mobility of pitches through a temperature range from ambient to 450°C . The change in mobility of proton of SCTP-2, PP-1, and CCP-2 is shown in **Figure 5-10(A)**, and (B) SCTP-2 + Petroleum Coke.

Figure 5-11(A) and **Figure 5-12(A)**, respectively. Each pitch (22 wt.%) was also mixed with 20-60 mesh size petroleum coke to study the interaction and wetting behavior between pitch and coke. The spectra of pitch+coke mixtures are shown in **Figure 5-10(B)**, and (B) SCTP-2 + Petroleum Coke.

Figure 5-11(B) and **Figure 5-12(B)** for SCTP-2, PP-1 and CCP-2, respectively. The shape of CCP-2 spectra looks more similar to those of PP-1. This is expected since

CCP-2 was isolated from co-coking overhead, which has been shown to be mostly petroleum-derived components.

Figure 5-10. High Temperature ^1H NMR Spectra at 100-450°C of (A) SCTP-2 only; and (B) SCTP-2 + Petroleum Coke.

Figure 5-11. High Temperature ^1H NMR Spectra at 100-450°C of (A) PP-1 only; and (B) PP-1 + Petroleum Coke

Figure 5-12. High Temperature ^1H NMR Spectra at 14-450°C of (A) CCP-2 only; and (B) CCP-2 + Petroleum Coke

Figure 5-13. Width at Peak Half-height ($\Delta H_{1/2}$) of CCP-2, PP-1 and SCTP-2 With and Without Petroleum Coke

The width at peak half-height ($\Delta H_{1/2}$) of each pitch sample was measured without considering if the spectrum has more than one peak. The variation in $\Delta H_{1/2}$ at different temperatures of all pitch samples is shown **Figure** . PP-1 and SCTP-2 show the same pattern of $\Delta H_{1/2}$, e.g. dropping dramatically from room temperature to $\sim 130^{\circ}\text{C}$, gradually decrease in $\Delta H_{1/2}$ until a minimum value is reached at about 200°C , then gradually increase in $\Delta H_{1/2}$ until the temperature is $\sim 300^{\circ}\text{C}$ and $\Delta H_{1/2}$ is then stabilized. It was anticipated that CCP-2 might also behave in a similar way, however, the initial temperature of the experiment was well above the glass transition temperature of the co-coking pitch. To collect a full range of $\Delta H_{1/2}$ of CCP-2, the sample would need to be cooled down to at least -50°C *in situ* while acquiring the spectra. The capability of the NMR spectrometer will be checked to see if this experiment can be done in the future.

A one-by-one comparison of “pitch only” and “pitch+coke” at different temperatures is shown in **Figure 5-14**. It can be seen that the $\Delta H_{1/2}$ of “SCTP-2 only” is much narrower than that of “SCTP-2+coke” as compared to PP-1 and CCP-2. This may indicate the level of interaction/mobility between pitch and coke. However, not many researchers have worked in this area and consequently more literature review and understanding of NMR are needed to interpret these results.

Figure 5-14. Comparison of High Temperature ^1H NMR Spectra between Pitch-only and Pitch + Coke at Different Temperatures (A) Sctp-2; (B) PP-1 and (C) CCP-2.

Solution State NMR

Solution state ^1H NMR spectra of CCP-2, PP-1 and Sctp-2 are shown in **Figure 5-15**. The aromatic band is in the range of 6-10 ppm and the aliphatic band is widely distributed in the ranges of 0.5-5 ppm. **Figure 5-15** and **Figure 5-16** show very small fraction of aliphatic hydrogen and carbon in Sctp-2, whereas PP-1 and CCP-2 show similar distribution of aromatic and aliphatic hydrogen and carbon. The bulk analysis NMR confirm that CCP-2 was mainly derived from petroleum compounds, i.e. major compounds were from the decant oil rather than coal. **Table 5-21** shows the aromatic and aliphatic hydrogen and carbon as calculated by integrating the solution state ^1H NMR and ^{13}C NMR spectra.

Table 5-21 Aromatic and Aliphatic Distribution of Pitches as Analyzed by Solution state ^1H and ^{13}C NMR.

<u>Solution state ^1H NMR</u>		
	<u>Aromatic H</u>	<u>Aliphatic H</u>
CCP-2	55.925	44.611
PP-1	56.433	43.412
Sctp-2	84.057	15.951
<u>Solution state ^{13}C NMR</u>		
	<u>Aromatic C</u>	<u>Aliphatic C</u>
CCP-2	85.105	14.895
PP-1	86.750	13.250
Sctp-2	97.033	2.967

Figure 5-15. Solution State ^1H NMR of CCP-2, PP-1 and SCTP-2.

Figure 5-16. Solution State ^{13}C NMR of CCP-2, PP-1 and Sctp-2.

Subtask 5.6: Manufacture and Testing of Carbon Artifacts

As we began to investigate the equipment that would be required to prepare and evaluate carbon artifacts properly for the industries that use them, it became apparent that a far more useful approach would be to develop working relationships with specific industrial partners. To that end we have been in discussions with Alcoa to prepare and test our first carbon artifacts. As stated earlier, a 20kg clean coal sample was prepared for 12 laboratory-scale delayed coker runs that will generate about 16 kg of coke. Alcoa requires about 5 kg of calcined coke of a very specific particle size distribution in order to prepare and test a series of carbon artifacts containing different percentages of binder pitch and anode butt material. Once we provide them with the calcined coke, they will use their R&D Carbon equipment to prepare 1:1000 scale baked anodes for a variety of tests that may include real helium density, bulk density, air reactivity, CO₂ reactivity, ash yield, major and trace elements, etc. At this time, the bulk sample of co-coke has been delivered to A.J. Edmond Co. to be calcined and sized for Alcoa. From this Penn State also expects to receive representative samples of both the green and calcined coke for evaluation and testing for Task 5.0. During the next performance period we will acquire equipment that will allow us to generate industry-scale test samples that can be evaluated on site or sent off to an appropriate laboratory for analysis. This is most important as we will be collecting and generation of at least two additional coals for the project and can not depend upon the good graces of Alcoa to continue to evaluate our cokes. Consequently, we will produce and test carbon artifacts in house i.e. carbon anodes, from the products of co-coking and compare the test results with the carbon artifacts made

from SCTP and PP. **Table 5-22** shows samples of carbon artifacts that will be produced for this study.

Table 5-22. Samples of Manufacturing of Carbon Artifacts

Pitch	Coke
SCTP	Commercial cokes
SCTP	Co-coking cokes
PP	Commercial cokes
PP	Co-coking cokes
Co-coking pitch	Commercial cokes

Future Work

1. Continue to evaluate techniques to generate a homogeneous carbon product from the co-coking of coal and petroleum residua.
2. Identify, collect and beneficiate two additional coals for co-coking using the techniques developed with the Pittsburgh seam FCE.
3. Continue to evaluate carbon quality with respect to existing markets, i.e., anode, electrode, direct reduction of iron, etc.
4. Complete the compositional analysis of all pitch samples.
5. Understand the wetting behavior between pitch and coke from the high temperature solid state ^1H NMR spectra.
6. Prepare new co-coking pitch samples using the new composite liquids from the 12 consecutive co-coker runs. A heat treatment may be applied to add more condensed aromatic compounds and increase the softening point of the sample to get a mass distribution closed to that of SCTP and PP.

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List of Acronyms and Abbreviations

1THQ	1,2,3,4-tetrahydroquinoline
5THQ	5,6,7,8-tetrahydroquinoline
AFOSR	Air Force Office of Scientific Research
API	American Petroleum Institute
BET	benzene/ethylbenzene/toluene surface area measurement
BT	benzothiophene
CFR	Cooperative Fuels Research
CCCFP	continuously closed cup flash point
CN	cetane number
DBT	dibenzothiophene
DCN	derived cetane number
DDC	Detroit Diesel Corporation
DDS	direct desulfurization
DHN	decahydronaphthalene
DHQ	decahydroquinoline
DMBP	dimethyl biphenyl
DMDBT	dimethyldibenzothiophene
DMDCH	dimethyl dicyclohexyl
DMN	dimethyl naphthalene
ECM	electronic control module
EGR	exhaust gas recirculation
EN	ethyl naphthalene
EPA	Environmental Protection Agency
EXAFS	Extended X-ray Absorption Fine Structure
FBP	final boiling point
FCC	fluid catalytic cracking
FID	flame ionization detector
FTIR	Fourier Transform Infrared
GC	gas chromatography
GCMS	gas chromatography-mass spectrometry
HCCI	homogeneous charge compression ignition
HDMDBT	hydrodimethyl dibenzothiophene
HDS	hydrodesulfurization
HDT	hydrotreated
HDY	hydrogenation
HM	H-mordenite
HPLC	high pressure liquid chromatography
HY	H Y-type zeolite
HYD	hydrogenation pathway
HZSM	H-synthetic zeolite material
IBP	initial boiling point
IC	internal combustion
INCA	a computer interface
IQT	ignition quality test

JP-900	jet fuel prototype stable to 900 F
LCO	light cycle oil
LDMS	laser desorption mass spectrometry
LHSV	liquid hourly space velocity
LTHDA	low temperature hydrotreating and dearomatization
MBP	methyl biphenyl
MCHT	methyl cyclohexyl toluene
MCM	mesoporous catalytic material
MN	methyl naphthalene
NTP	normal temperature and pressure
PARC	Pennsylvania Applied Research Corporation
PB	propyl benzene
PCH	propyl cyclohexane
PCHE	propyl cyclohexene
PP	petroleum pitch
PSU	Penn State University
Py-	pyrolysis-
RCO	refined chemical oil
RSF	relative severity factor
SCTP	standard coal tar pitch
SI	spark ignited
SpGr	specific gravity
SwRI	Southwest Research Institute
THT	tetrahydrothiophene
TLP	total liquid product
TOS	time on stream
WHSV	weight hourly space velocity
XPS	x-ray photoelectron spectroscopy